

## Cation Effects in the Reduction of Stilbenes in Liquid Ammonia

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The reductive isomerization of *cis*-stilbene into *trans*-stilbene in liquid ammonia at  $-38\text{ }^{\circ}\text{C}$  was investigated in the presence of various cations. Cyclic voltammetry showed that isomerization was favored when going from  $\text{Li}^+ \approx \text{Na}^+$  to  $\text{K}^+$  and  $\text{Mg}^{2+}$ . This observation was interpreted by a simple model involving rough approximations and association within dianionic species only. This model showed that the isomerization process was mainly governed by the isomerization reaction of the *cis*-stilbene dianion, the disproportionation reaction acting as a preequilibrium. When going from  $\text{Li}^+ \approx \text{Na}^+$  to  $\text{K}^+$  and  $\text{Mg}^{2+}$ , disproportionation was favored and isomerization on the elemental step disfavored, which pointed out the predominant role of disproportionation over isomerization. Consequently, the isomerization of  $\text{CS}^{2-}$  was supposed to proceed within the ion pair and the stronger the interaction between the cation and the dianion, the slower the rotation around the C–C bond.

### Introduction

The reductive behavior of phenyl-substituted ethylenes is well documented in the literature. Two significant factors have been particularly studied: the influence of the nature of the substituents on the reduction process and the disproportionation reaction of the anion-radical obtained upon the first electron transfer.<sup>1</sup>

The influence of the nature of the substituents on the electrochemical reduction of phenyl-substituted ethylenes in aprotic solvents such as DMF was recognized early by polarography<sup>2–5</sup> as well as by cyclic voltammetry<sup>6–8</sup> and confirmed by systematic studies.<sup>9–11</sup> Two monoelectronic reduction peaks or one bielectronic peak may be observed, depending on the compound structure and the solvent.<sup>2,4,6–8,12,13</sup> Direct 2-electron-transfer reactions are also reported upon oxidation, for example for tetra-*p*-anisylethylene.<sup>14</sup>

Disproportionation of the anion-radical has been investigated thoroughly under chemical or electrochemical conditions in the case of the tetraphenylethylene anion-radical ( $\text{TP}^{\bullet-}$ ):

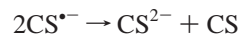


It was shown to be strongly dependent on the medium and particularly on ion-pair interactions.<sup>1,8,15–19</sup>

In the particular case of *cis*-stilbene (CS), reduction is accompanied by isomerization into the *trans* derivative. Electron-transfer-induced reduction of *cis*-stilbene has been studied by different groups since it was first observed by Hoijsink et al.<sup>20</sup> and later by Doran et al.<sup>21</sup>

Szwarc et al. have investigated the kinetics of the reduction of *cis*-stilbene by radical-anions.<sup>22–25</sup> They have shown that isomerization of *cis*-stilbene is not a unimolecular reaction converting directly  $\text{CS}^{\bullet-}$  into  $\text{TS}^{\bullet-}$  but that it involves disproportionation of  $\text{CS}^{\bullet-}$  and proceeds on the level of dianions along different possible reactions. Jensen et al. were the first electrochemists to observe and discuss the electrochemically mediated *cis*-to-*trans* conversion of stilbene in DMF by cyclic voltam-

metry.<sup>26</sup> By a quantitative electrolysis-ESR method, Nozaki et al. have also shown that in DMF in the absence of electron donors and alkali-metal cations, isomerization of  $\text{CS}^{\bullet-}$  proceeds through  $\text{CS}^{2-}$  and that its rate-determining step is the disproportionation of  $\text{CS}^{\bullet-}$ :<sup>27</sup>



Disproportionation appears therefore as a common feature in the reduction of phenyl-substituted ethylenes. A high rate of disproportionation was indeed observed for 1,2-diphenylcyclohexene, which cannot isomerize into the *trans* form due to the rigidity of the cyclohexene ring.<sup>28</sup>

The existence of  $\text{CS}^{\bullet-}$  as an intermediate in the reduction of *cis*-stilbene is therefore difficult to evidence experimentally. It could be demonstrated by the ESR resolved spectrum of  $\text{CS}^{\bullet-}$ ,<sup>26,27</sup> its optical spectrum obtained from an irradiated solution<sup>29</sup> or by flash photolysis<sup>25</sup> or pulse radiolysis;<sup>26</sup> they all are different from those of  $\text{TS}^{\bullet-}$ .

In this paper, we have then attempted to demonstrate the effect of ion association on the reduction mechanism (thermodynamics and kinetics) of stilbene in liquid  $\text{NH}_3$ . Indeed, theoretical models have been recently proposed to rationalize the solvation and cation influence on the  $E^{\circ}$  of redox systems in DMF and liquid ammonia.<sup>30</sup> We have used 4 different electrolytes:  $\text{LiBF}_4$ ,  $\text{NaBF}_4$ ,  $\text{KBF}_4$ , and  $\text{Mg}(\text{BF}_4)_2$ .  $\text{NH}_3$  was chosen as the solvent since it is stable in the presence of strong bases contrarily to organic solvents such as acetonitrile. DMF could also have been used, but  $\text{NH}_3$  was preferred since its stability in basic media is higher than that of DMF. Actually, in liquid  $\text{NH}_3$ , it is possible to observe the reversibility of redox systems involving strong bases, even in the presence of known Lewis acids such as  $\text{Li}^+$  and  $\text{Mg}^{2+}$ . Liquid  $\text{NH}_3$  should then be the most appropriate solvent for the investigation of disproportionation reactions in the presence of large amounts of such acidic cations. Electrolytes with the same anionic part were preferred since they allowed the evidence of cation effects irrespective of the nature of the associated anion; the tetrafluoroborate anion was chosen since magnesium tetrafluoroborate is one of the few soluble magnesium salts in liquid  $\text{NH}_3$ .<sup>31</sup>

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## 2. Experimental Section

The reagents were purchased from Aldrich and used without further purification. Liquid ammonia was purchased from Air Liquide.  $\text{Mg}(\text{BF}_4)_2$  was prepared in situ by reduction of  $\text{NH}_4\text{BF}_4$  at the cathode.<sup>31</sup>

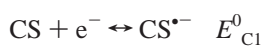
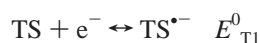
The electrochemical cell was filled with 80 mL of liquid ammonia whose temperature was maintained at  $-38^\circ\text{C}$  with a cryocooler (Bioblock scientific) and lithium, sodium, potassium, or magnesium tetrafluoroborates were used as electrolytes. The reference electrode was a  $\text{Ag}|0.01\text{ M Ag}^+$  electrode.<sup>32</sup> The working electrode was either a gold disk ( $\phi = 0.5\text{ mm}$ ), or a mercury drop electrode coated on a gold disk ( $\phi = 0.5\text{ mm}$ ), or a glassy carbon disk ( $\phi = 0.88\text{ mm}$ ). A platinum wire worked as auxiliary electrode. Cyclic voltammograms were recorded using a CHI660A potentiostat (CH Instruments, IJ Cambria Scientific, Burry Port, UK).

Voltammograms were simulated with Digisim software (BAS Technicol, UK).

## 3. Experimental Investigation by Cyclic Voltammetry

**3.1. Cyclic Voltammetry of *trans*- and *cis*-Stilbenes in Liquid  $\text{NH}_3$ .** Reduction of *trans*- and *cis*-stilbene is characterized by 2 successive systems in most organic solvents.<sup>26</sup> The first system corresponds to the reduction of *trans* (or *cis*)-stilbene into its anion-radical:

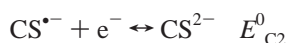
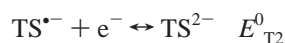
### System I



It is generally reversible since  $\text{TS}^{\bullet-}$  and  $\text{CS}^{\bullet-}$  are weak bases.

The second system corresponds to the formation of the *cis* (or *trans*) dianion:

### System II



It is irreversible in aprotic organic solvents since  $\text{TS}^{2-}$  and  $\text{CS}^{2-}$  are strong bases, which protonate readily in these media.<sup>1</sup> However, it was possible to observe the reversibility of System II for solutions of both *cis*- and *trans*-stilbenes in liquid  $\text{NH}_3$  whatever the sweep rate in the absence of acidic impurities (such as  $\text{H}_2\text{O}$ ).

Since experimental observations were always the same with  $\text{LiBF}_4$  and  $\text{NaBF}_4$ , we have not reported in the following the experimental data obtained with  $\text{LiBF}_4$ .

In the case of *trans*-stilbene, voltammetry was not performed directly on the neutral compound since *trans*-stilbene is poorly soluble in liquid  $\text{NH}_3$ . This drawback was circumvented by performing voltammetry of the corresponding anion-radical. The latter was obtained by reducing *trans*-stilbene by the stoichiometric amount of the alkali metal.

With  $\text{Mg}(\text{BF}_4)_2$  as the electrolyte, that procedure could not be carried out since magnesium is not directly soluble in liquid ammonia.<sup>31</sup> Another procedure was tried, that consisted of adding *trans*-stilbene to a solution of magnesium. Unfortunately, that procedure resulted in a perturbed voltammogram that was useless. Such behavior could be explained by (i) the slow reductive dissolution of *trans*-stilbene, (ii) the subsequent

reduction of the radical-anion by the excess of electrons, followed by (iii) protonation due to the higher acidity of  $\text{NH}_3$  in the presence of magnesium cations.

Finally, it was possible to obtain a *trans*-stilbene radical anion solution by electrolyzing a solution of *cis*-stilbene in the presence of  $\text{Mg}(\text{BF}_4)_2$  as the electrolyte. The solution was not very stable, and the stilbene derivative was transformed into a non electroactive compound within few minutes. Therefore the  $\text{TS}^{\bullet-}$  content of the solution analyzed in Figure 1c is not known. The decomposition of the *trans*-stilbene radical anion has not been investigated further, but it could be a consequence of the instability of the dianion  $\text{TS}^{2-}$  due to enhanced acidity of  $\text{NH}_3$  in the presence of magnesium cations.

The *trans*-stilbene dianion may be obtained at some point of the electrolysis by direct reduction at the cathode or by disproportionation of  $\text{TS}^{\bullet-}$  anion-radical.

The enhanced acidity of  $\text{NH}_3$  in the presence of magnesium cations has already been reported.<sup>33</sup> For example, the anion of triphenylmethane ( $\Phi_3\text{CH}$ ), which can be obtained either by reduction of  $\Phi_3\text{CCl}$  or  $\Phi_3\text{CH}$  by the stoichiometric amount of solvated electrons, is not stable in the presence of magnesium cations while it is in the presence of alkali cations: once prepared by reaction with the stoichiometric amount of reactant, the red color of a  $10^{-2}\text{ M}$  solution vanishes in  $\sim 1\text{ min}$ .

The cyclic voltammograms of *cis* (or *trans*)-stilbene at  $0.1\text{ V s}^{-1}$  are represented in Figure 1a–c, respectively, with  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$  as the cation of the electrolyte. In the latter case, a glassy carbon electrode was used since glassy carbon exhibits a higher cathodic surtension for proton discharge than gold.<sup>33</sup> The higher currents observed with the magnesium cation result from the larger diameter of the electrode ( $0.88\text{ mm}$  instead of  $0.5\text{ mm}$ ). For *cis*-stilbene, potentials were scanned negatively from  $\sim -1.3\text{ V/Ag/Ag}^+$  to  $\sim -2.3\text{ V/Ag/Ag}^+$  and back. For *trans*-stilbene, since only the solution of the radical-anion was available, potentials were scanned positively from  $\sim -1.9\text{ V/Ag/Ag}^+$  to  $\sim -1.3\text{ V/Ag/Ag}^+$ , then negatively to  $\sim -2.3\text{ V/Ag/Ag}^+$ , and at last positively to the initial potential value. The two expected systems could be seen and different observations were made depending on the nature of the cation of the electrolyte.

### 3.2. Electrochemistry of the *trans*-Stilbene Anion-Radical.

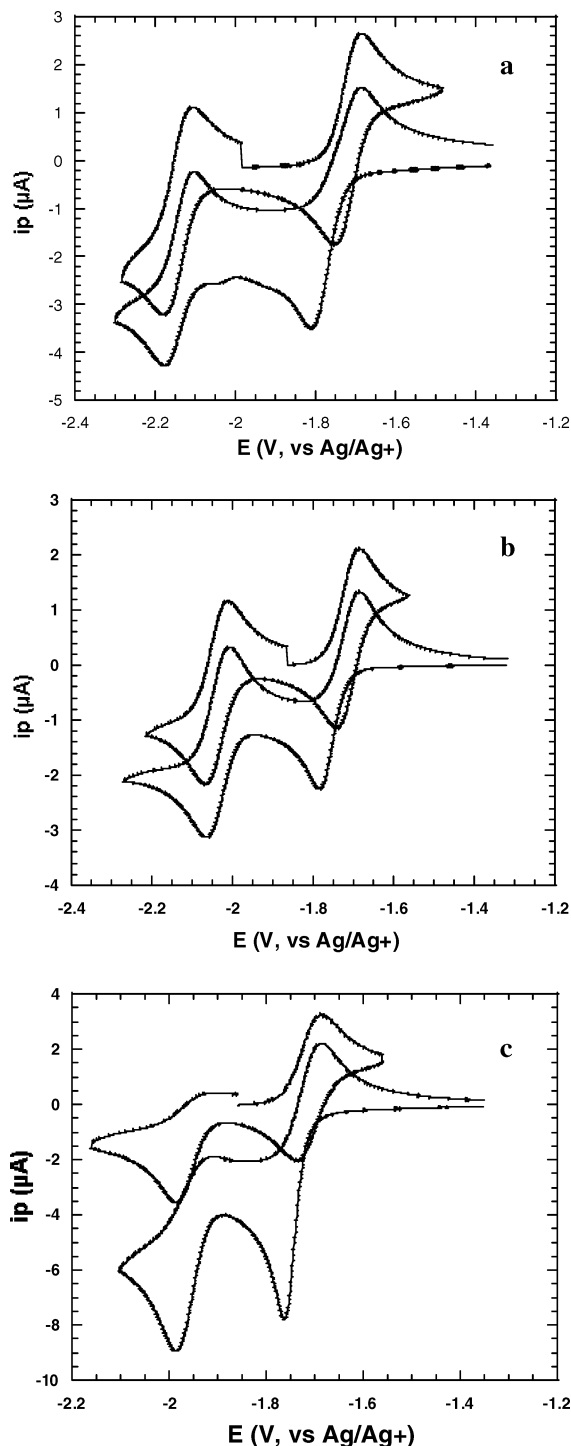
**3.2.1 Oxidation of the *trans*-Stilbene Anion-Radical.** The first redox system (system I) observed when oxidizing *trans*-stilbene anion-radical did not change when changing the electrolyte or the sweep rate. The electrochemical characteristics of a nernstian system at  $-40^\circ\text{C}$  were observed: a half-width of  $48\text{ mV}$  on the anodic and cathodic peaks (for Li, Na, K) and a difference of  $50\text{ mV}$  between the anodic and cathodic peaks (for Li, Na, K) over a range of scan rates comprised between  $0.1\text{ V/s}$  and  $1\text{ V/s}$ . The standard potential of system I was estimated as the mean of the anodic and cathodic peaks and for any cation denoted  $\text{M}^{z+} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{or } \text{Mg}^{2+}$ :

$$E_{\text{T1}}^0(\text{TS/TS}^{\bullet-}, \text{M}^{z+}) = -1.715 \pm 0.005\text{ V/Ag/Ag}^+$$

The simulation of the experimental voltammograms for scan rate ranging from  $0.1\text{ V/s}$  to  $5\text{ V/s}$  (Digisim) allowed us to estimate the electron-transfer rate constant for the oxidation of the anion-radical of the *trans* isomer  $k_s(\text{TS}, \text{M}^{z+})$ , and its diffusion coefficient,  $D_s(\text{CS}, \text{M}^{z+})$ :

$$k_s(\text{TS}, \text{M}^{z+}) = 0.2\text{ cm s}^{-1}$$

$$D_s(\text{TS}, \text{M}^{z+}) = 2.7 \times 10^{-5}\text{ cm}^2\text{ s}^{-1}$$



**Figure 1.** Cyclic voltammetry of *trans*- and *cis*-stilbene in liquid  $\text{NH}_3$  at  $-38\text{ }^\circ\text{C}$ .  $v$  (sweep rate =  $0.1\text{ V s}^{-1}$ ). Bottom: *cis*-stilbene; Top: *trans*-stilbene. Electrolytes, concentrations, and electrodes: (a)  $0.148\text{ M NaBF}_4$ , [*trans*-stilbene $^{\bullet-}$ ] =  $3.00\text{ mM}$ , [*cis*-stilbene] =  $3.30\text{ mM}$ , gold disk electrode ( $\phi = 0.5\text{ mm}$ ); (b)  $0.132\text{ M KBF}_4$ , [*trans*-stilbene $^{\bullet-}$ ] =  $2.00\text{ mM}$ , [*cis*-stilbene] =  $2.00\text{ mM}$ , gold disk electrode ( $\phi = 0.5\text{ mm}$ ); (c)  $0.105\text{ M Mg(BF}_4)_2$ , [*trans*-stilbene $^{\bullet-}$ ] =  $1.70\text{ mM}$ , [*cis*-stilbene] =  $2.02\text{ mM}$ , glassy carbon electrode ( $\phi = 0.88\text{ mm}$ ).

We have measured in liquid  $\text{NH}_3$  the first standard reduction potentials of a lot of reversible redox systems (neutral/radical-anion) and shown that they did not change when varying the electrolyte cation ( $\text{M}^{z+} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Mg}^{2+}$ ). These systems and their first standard reduction potentials vs  $\text{Ag/Ag}^+$  are the following: *trans*-1,2-bis-4-pyridylethylene ( $-1.105\text{ V}$ ), terephthalonitrile ( $-1.035\text{ V}$ ), quinoxalin ( $-1.085\text{ V}$ ), phthalonitrile

( $-1.13\text{ V}$ ), cyano-4-pyridyl ( $-1.25\text{ V}$ ), cyano-2-pyridyl ( $-1.43\text{ V}$ ), benzonitrile ( $-1.785\text{ V}$ ) and also *trans*-stilbene ( $-1.715\text{ V}$ ) as mentioned above. The absence of cation influence on electrochemical or spectroscopic data has already been observed for anionic species such as anion-radicals<sup>34,35</sup> and solvated electrons<sup>36</sup> in  $\text{NH}_{3,l}$ . Owing to the high cation solvating power of  $\text{NH}_{3,l}$  ( $\text{DN} = 50$ <sup>37</sup>), it may be expected that anion-radicals, if they do, form loose ion pairs with the different solvated cations. Formation of loose pairs of solvated ions in liquid ammonia is in agreement with Raman spectroscopy measurements that have demonstrated that tighter (contact or solvent-shared) ion pairs, with an association constant about  $10\text{ M}^{-1}$ , are not preponderant in liquid ammonia.<sup>37</sup>

**3.2.2. Reduction of the *trans*-Stilbene Anion-Radical.** The second system (system II) observed at more negative potentials corresponds to the reduction of the *trans*-stilbene anion-radical. It depended on the nature of the electrolyte. It remained Nernstian with alkali tetrafluoroborates as electrolytes: a half-width of  $48\text{ mV}$  at the anodic and cathodic peaks and a difference of  $50\text{ mV}$  between the anodic and cathodic peaks were observed for  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$ . The standard reduction potential of system II, estimated as the mean of the anodic and cathodic peaks, increased from  $\text{Li}^+$  and  $\text{Na}^+$  to  $\text{K}^+$ :

$$E_{\text{T}_2}^0(\text{TS}^{\bullet-}/\text{TS}^{2-}, \text{Li}^+, \text{Na}^+) = -2.14 \pm 0.005\text{ V/Ag/Ag}^+$$

$$E_{\text{T}_2}^0(\text{TS}^{\bullet-}/\text{TS}^{2-}, \text{K}^+) = -2.035 \pm 0.005\text{ V/Ag/Ag}^+$$

The intensity of the second peak was about the same as that of the first peak for any alkali cation, as expected.

In the presence of  $\text{Mg(BF}_4)_2$ , the poor reversibility of the second system (system II, Figure 1c) could be noticed; it should be due to the protonation of the dianion of stilbene, which should be easier in liquid  $\text{NH}_3$  in the presence of a soluble magnesium salt than in the presence of an alkali metal as mentioned above.<sup>33</sup> The reversibility of system II in the presence of  $\text{Mg(BF}_4)_2$  could be obtained at higher scan rates and the standard potential of the second system could be determined:

$$E_{\text{T}_2}^0(\text{TS}^{\bullet-}/\text{TS}^{2-}, \text{Mg}^{2+}) = -1.96\text{ V} \pm 0.005\text{ V/Ag/Ag}^+$$

From the variation of the anodic to cathodic peak current ratio with the scan rate, one could estimate the apparent first-order rate constant for the disappearance of  $\text{TS}^{2-}$  by protonation in the magnesium solution. Depending on the water content of the solution it varied within  $2$  and  $10\text{ s}^{-1}$ . As discussed above, the instability of  $\text{TS}^{2-}$  may explain the low stability of  $\text{TS}^{\bullet-}$  solution in the presence of magnesium.

The different values of the standard reduction potentials involved in the reduction of *trans*-stilbene are gathered in Table 1 together with the resulting calculated constants of  $\text{TS}^{\bullet-}$  disproportionation:



The diffusion limit rate constant in liquid ammonia at  $-38\text{ }^\circ\text{C}$  was taken as  $k_{\text{dif}} = 3 \times 10^{10}\text{ M}^{-1}\text{ s}^{-1}$ .<sup>38</sup> This value, which appears large, particularly by considering that the temperature is low, results from the low viscosity of liquid ammonia:  $\eta_{\text{NH}_3} = 0.27\text{ cp}$  at  $-40\text{ }^\circ\text{C}$ ,<sup>36</sup> that can be compared for example to the viscosity of DMF at  $+20\text{ }^\circ\text{C}$ ,  $\eta_{\text{DMF}} = 0.92\text{ cp}$ .<sup>39</sup>

The values of the standard reduction potentials show that reduction of  $\text{TS}^{\bullet-}$  into  $\text{TS}^{2-}$  becomes easier when going from  $\text{Li}^+$  or  $\text{Na}^+$  to  $\text{K}^+$  and  $\text{Mg}^{2+}$ ; concomitantly, disproportionation of  $\text{TS}^{\bullet-}$  gets more favored. Similar cation effect was also

**TABLE 1: Thermodynamics Values for the Reduction of of *trans*- and *cis*-Stilbene**

electrolyte	$E^0_{T1} TS/TS^{•-}$	$E^0_{T2} TS^{•-}/TS^{2-}$	$K_{disp,TS,M.} = \exp(-F\Delta E^0/RT)$ $TS^{•-} \leftrightarrow TS^{2-} + TS$	$k_{disp} (M^{-1} s^{-1})$	$E^0_{C1} CS/CS^{•-}$
LiBF <sub>4</sub>	-1.71 <sub>5</sub> <sup>a</sup>	-2.14 <sup>a</sup>	$8.0 \times 10^{-10}$	23	-1.76 <sub>5</sub> <sup>a</sup>
NaBF <sub>4</sub>	-1.71 <sub>5</sub> <sup>a</sup>	-2.14 <sup>a</sup>	$8.0 \times 10^{-10}$	23	-1.76 <sub>5</sub> <sup>a</sup>
KBF <sub>4</sub>	-1.71 <sub>5</sub> <sup>a</sup>	-2.03 <sub>5</sub> <sup>a</sup>	$1.4 \times 10^{-7}$	$4.1 \times 10^3$	-1.76 <sub>5</sub> <sup>b</sup>
Mg(BF <sub>4</sub> ) <sub>2</sub>	-1.71 <sub>5</sub> <sup>a</sup>	-1.96 <sup>a</sup>	$5.5 \times 10^{-6}$	$1.6 \times 10^5$	-1.76 <sub>5</sub> <sup>b</sup>

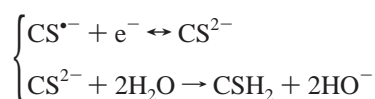
<sup>a</sup> Direct experimental determination. <sup>b</sup> Assumed to be equal to the value measured in the presence of Li<sup>+</sup> and Na<sup>+</sup>.

observed for other reversible redox systems (anion-radical/dianion) in NH<sub>3</sub>. Changing Na<sup>+</sup> into Li<sup>+</sup> did not affect the  $E^0$ , but using K<sup>+</sup> led to a potential shift in the positive direction, and Mg<sup>2+</sup> induced a much higher potential shift: *trans*-1,2-bis-4-pyridylethylene ( $E^0_{2-/•-} - E^0_{•-/0} = -0.38$  (Na<sup>+</sup>, Li<sup>+</sup>),  $-0.32$  (K<sup>+</sup>),  $-0.20$  (Mg<sup>2+</sup>) V), azobenzene ( $E^0_{2-/•-} - E^0_{•-/0} = -0.68$  (Na<sup>+</sup>, Li<sup>+</sup>),  $-0.55$  (K<sup>+</sup>),  $-0.48$  (Mg<sup>2+</sup>) V) and *trans*-stilbene ( $E^0_{2-/•-} - E^0_{•-/0} = -0.41_5$  (Na<sup>+</sup>, Li<sup>+</sup>),  $-0.32$  (K<sup>+</sup>),  $-0.22$  (Mg<sup>2+</sup>) V). Those potential dependencies reflect ion association between the dianionic species and the different cations of the electrolyte. Those trends show that tighter ion pairs are formed with more charged ions such as di-ions (i.e., dianions and Mg<sup>2+</sup>) that are more prone to ion-pairing.<sup>40</sup> Among the alkalis, the Li<sup>+</sup> and Na<sup>+</sup> cations if they are associated with TS<sup>2-</sup> are still strongly solvated in the ion pairs formed with the dianionic species, as no difference is observed when changing Li<sup>+</sup> into Na<sup>+</sup>. On the other hand, K<sup>+</sup> and especially Mg<sup>2+</sup> are associated more tightly with TS<sup>2-</sup>. Those cations may loose part of their solvation shell in the ion pair.

**3.3. Reduction of *cis*-Stilbene.** The two reduction systems of a solution of *cis*-stilbene at 0.1 V s<sup>-1</sup> depended on the nature of the electrolyte.

At 0.1 V s<sup>-1</sup>, on the first cyclic voltammogram of a solution of *cis*-stilbene, whatever the electrolyte, the first system showed oxidation waves on the reverse scan (cf Figure 1a–c). However, only the first reduction peak could be attributed to *cis*-stilbene and its anodic counterpart coincided with that observed for the *trans*-stilbene radical anion oxidation. Likewise, the second system (system II) corresponded to that observed during the *trans*-stilbene radical anion reduction, it was reversible for LiBF<sub>4</sub>, NaBF<sub>4</sub>, or KBF<sub>4</sub> and reflected partial protonation of TS<sup>2-</sup> in Mg(BF<sub>4</sub>)<sub>2</sub> solution.

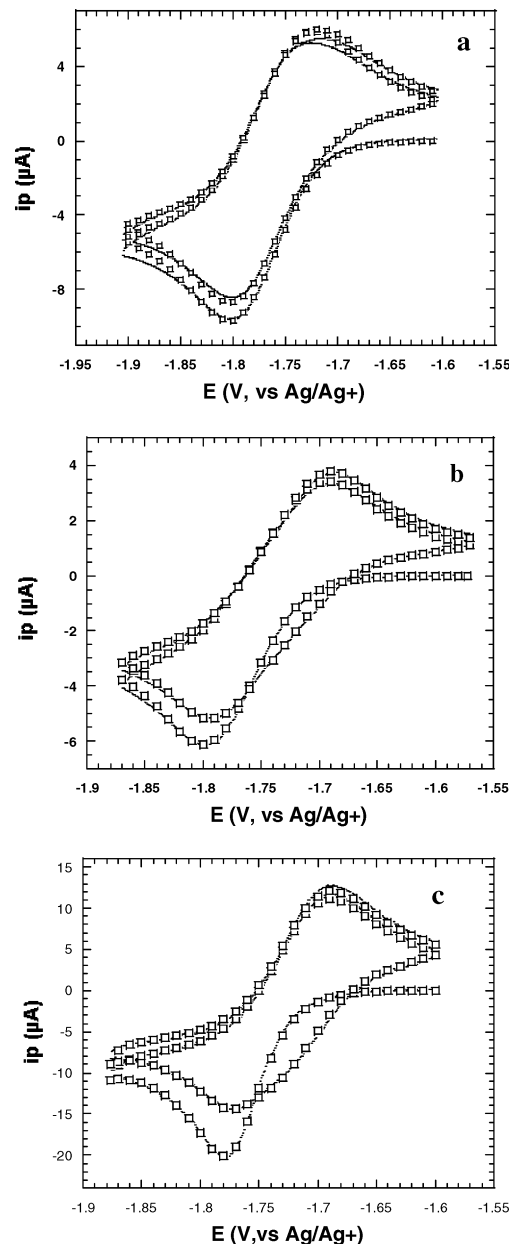
Protonation was also evidenced to a slight extent with NaBF<sub>4</sub> as the electrolyte in the presence of a small amount of residual water. In that case (Figure 1a), we have observed a reduction prewave at a more positive potential than that of system II that we have attributed to the following system:



In the absence of residual water, system II was reversible for both *cis*- and *trans*-stilbene solutions with both NaBF<sub>4</sub> and KBF<sub>4</sub> as electrolytes, as could be seen in Figure 1b that was obtained in an anhydrous solvent.

The peak characteristics of the first system—peak potential, half-width and current—depended on the electrolyte. Its half-width decreased from 46 mV to 37 mV and 26 mV as the peak height increased when going from NaBF<sub>4</sub> to KBF<sub>4</sub> and Mg(BF<sub>4</sub>)<sub>2</sub>. Moreover, even in the presence of an alkali cation, the intensity of the first reduction peak was always higher than that of the second peak, as expected when a chemical reaction has to be taken into account.

Successive cyclic voltammograms of the first reduction system of *cis*-stilbene at 1 V s<sup>-1</sup> are represented in Figure 2a–



**Figure 2.** Cyclic voltammetry of *cis*-stilbene in liquid NH<sub>3</sub> at  $-38$  °C.  $v$  (sweep rate) = 1 V s<sup>-1</sup> on a gold disk electrode ( $\phi = 0.5$  mm). Electrolytes, concentrations, and electrodes: idem Figure 1. Solid lines: experimental data. Dots: simulations according to mechanism B.

c, respectively, with Na, K, and Mg as the cation of the electrolyte. In the three cases, the reduction wave observed at the second scan was different from that at the first scan: a shoulder appeared at a more positive potential than the peak potential at the first scan and an overlap of the first and second scan reduction waves could be noticed. The intensity of the shoulder and the importance of the overlap increased from NaBF<sub>4</sub> to KBF<sub>4</sub> and Mg(BF<sub>4</sub>)<sub>2</sub> and by lowering the scan rate.



In agreement with the voltammograms observed at  $0.1 \text{ V s}^{-1}$ , such a behavior could be attributed to the appearance of the system of *trans*-stilbene.

With  $\text{NaBF}_4$  as the electrolyte, no presence of the *trans* isomer could be detected at scan rates higher than  $1 \text{ V s}^{-1}$ . The simulation of the voltammograms obtained at scan rates higher than  $1 \text{ V/s}$  (Digisim) allowed us to estimate the standard first reduction potential of the *cis* isomer,  $E_{\text{Cl}}^0(\text{CS}/\text{CS}^{\bullet-}, \text{Na}^+)$ , its electron-transfer rate constant,  $k_s(\text{CS}, \text{Na}^+)$ , and its diffusion coefficient,  $D_s(\text{CS}, \text{Na}^+)$ :

$$E_{\text{Cl}}^0(\text{CS}/\text{CS}^{\bullet-}, \text{Na}^+) = -1.765 \pm 0.005 \text{ V/Ag/Ag}^+ \text{ V/Ag/Ag}^+$$

$$k_s(\text{CS}, \text{Na}^+) = 0.15 \text{ cm s}^{-1}$$

$$D_s(\text{CS}, \text{Na}^+) = 2.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

We believe it is difficult to discriminate whether loose ion pairs are formed with anion-radicals in liquid ammonia. Anyway, it is legitimate to assume that, as it has been observed for the *trans* isomer,  $E_{\text{Cl}}^0(\text{CS}/\text{CS}^{\bullet-})$  did not depend on the cation of the electrolyte:

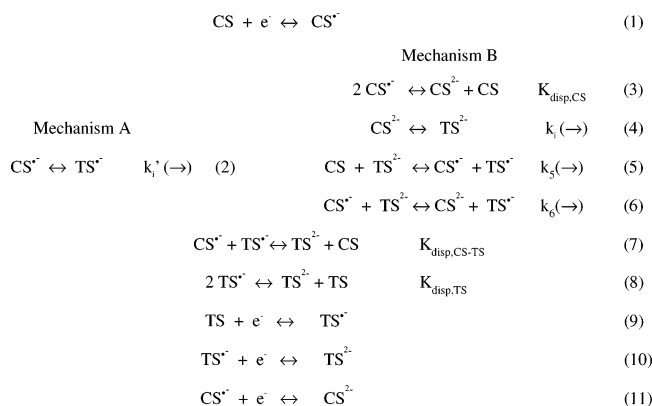
$$E_{\text{Cl}}^0(\text{CS}/\text{CS}^{\bullet-}, \text{M}^{\text{z}+}) = -1.765 \pm 0.005 \text{ V/Ag/Ag}^+$$

#### 4. Interpretation and Proposition of a Reduction Mechanism for *cis*-Stilbene

**4.1. Possible Reduction Mechanisms for *cis*-Stilbene.** The latter results indicate that *cis*-stilbene isomerized into *trans*-stilbene under a one electron transfer in liquid  $\text{NH}_3$  in the presence of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , or  $\text{Mg}^{2+}$  cations as already observed in organic aprotic solvents. We have observed that the electrolyte cation affected the thermodynamics of the disproportionation reaction and also of the isomerization process.

Since it is difficult to quantify ion association, we have simplified the reaction mechanism and have not taken into account ion-pairing effects. Then, we may postulate that isomerization occurs at the level of the anion-radical,  $\text{CS}^{\bullet-}$ , or the dianion,  $\text{CS}^{2-}$ , intermediates according to, respectively, mechanism A and mechanism B (Scheme 1):

#### SCHEME 1. Possible Reduction Mechanisms for *cis*-Stilbene



In the case of the magnesium solutions, we have not taken into account the protonations of the dianions as they may be too slow to compete efficiently with the other chemical reactions in which the dianions are involved (homogeneous electron transfer or isomerization).

In mechanism A, the reaction kinetics depends only on the radical-anion isomerization reaction 2. In mechanism B, it depends on both the disproportionation reaction 3 and the dianion isomerization reaction 4. Therefore, in the first case, the kinetics should be governed by  $k_i'$  and in the second case by  $K_{\text{disp,CS}}$  and  $k_i$ .

The half-width of the first reduction system of *cis*-stilbene decreased from 46 mV to 37 mV and 26 mV when going from  $\text{Li}^+$  or  $\text{Na}^+$  to  $\text{K}^+$  and  $\text{Mg}^{2+}$ , while the peak current increased when going from  $\text{Li}^+$  to  $\text{Mg}^{2+}$  at  $1 \text{ V/s}$ . The narrowing and increase of the peak are far too important to account for a simple control by a first-order reaction as would be expected in mechanism A. Indeed the smallest half-width expected would be 38 mV. Thinner and greater peaks are expected for mechanisms that are kinetically limited by second-order reactions such as dimerization or DISP reactions.<sup>41</sup> The peaks shape is then more in favor of mechanism B than of mechanism A. Since in addition, only the dianion formation is sensitive to cations, the isomerization process, which is cation-dependent, should occur at the level of the dianion rather than the radical-anion. We have then assumed that mechanism B was favored as already stated in organic aprotic solvents<sup>22–27</sup> and that disproportionation of  $\text{CS}^{\bullet-}$  was favored by the association of  $\text{CS}^{2-}$  with  $\text{Mg}^{2+}$  and to a lesser extent with  $\text{K}^+$ .

**4.2. Simulations.** To test mechanism B, we have simulated the voltammograms of the first reduction system of *cis*-stilbene by considering the whole set of reactions (except reaction 2). For a more simple simulation of the voltammograms, we have not taken specifically into account ion association reactions since we did not want to deal with a great number of unknown thermodynamics and kinetics reaction rate constants. The ion-sensitiveness was introduced by using the cation dependence of the standard reduction potential of *trans*- and *cis*-stilbene.

To perform the simulation, it was necessary to know the values of the different standard reduction potentials involved and therefore to estimate the value of  $E_{\text{C2}}^0$  in the presence of the different electrolytes. Indeed, once  $E_{\text{C2}}^0$  was known, the rate constants of the different homogeneous electron-transfer reactions could be evaluated.

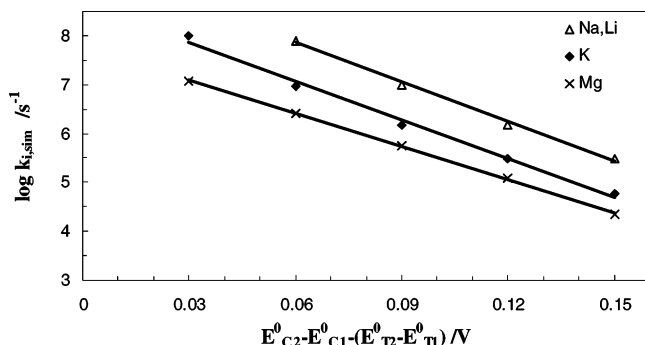
**4.2.1. Rate Constants Evaluation.** The rate constants used for the simulations of the backward and forward reactions of equilibria 5, 7, and 8 were estimated a priori, for each value of  $E_{\text{C2}}^0$ , by holding the fastest reaction under diffusion control  $k = k_{\text{dif}} = 3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , and evaluating the slowest one from  $k_f/k_b = K_{\text{eq}}$ , where  $k_f$  and  $k_b$  are the forward and backward reactions of the equilibrium whose constant is  $K_{\text{eq}}$ , that may be obtained, in a first approximation, from the different standard reduction potentials.

Because of the small value of the difference  $E_{\text{T2}}^0 - E_{\text{C2}}^0$ , reaction 6 should be under a mixed kinetic control by formation and breaking of the encounter complexes (diffusion control) and the electron-transfer step (activation control). Therefore we could deduce  $k_6$  and  $k_{-6}$  from a combination of

$$k_6/k_{-6} = \exp(-F(E_{\text{T2}}^0 - E_{\text{C2}}^0)/RT)$$

$$1/k_6 = 1/k_{\text{dif}} + 1/(k_{\text{exc}} \exp(-F(E_{\text{T2}}^0 - E_{\text{C2}}^0)/RT)) + 1/(k_{\text{dif}} \exp(-F(E_{\text{T2}}^0 - E_{\text{C2}}^0)/RT))$$

where  $k_{\text{exc}}$  is the exchange rate constant of reaction 6 at zero driving force. The latter term usually takes into account, through Marcus theory, the reorganization involved in the electron transfer within the caged compounds. We have postulated that this reorganization lead to an exchange rate constant of the order



**Figure 3.** Variations of the simulated values of  $k_{i,\text{sim}}$  with,  $E^0_{\text{C2}}$ , the standard reduction potential of  $\text{CS}^{\bullet-}$ .

of  $k_{\text{exc}} = 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , a classical value for electron transfer with organic molecules that develop low reorganization. We could then estimate the values of the homogeneous electron-transfer rate constants  $k_6$  and  $k_{-6}$ .

Once these rate constants were evaluated, the simulation depended mainly on  $k_i$  and  $E^0_{\text{C2}}$ . The simulation procedure consisted of obtaining the value of the isomerization rate constant,  $k_{i,\text{sim}}$ , for a given value of  $E^0_{\text{C2}}$ , that produced a simulated CV that fitted the experimental CV for the different scan rates (comprised between 0.1 V/s and 10 V/s), for each electrolyte. Figure 2 presents some fits (dots) of the experimental CV (solid lines).

**4.2.2. Incidence of  $E^0_{\text{C2}}$ .** First, we have assumed that the two different stilbene dianions developed similar interactions with cations, as the corresponding anion-radicals did. The potential difference between the first and second reduction systems should then be about the same for *cis*- and *trans*-stilbene ( $E^0_{\text{C1}} - E^0_{\text{C2}} \sim E^0_{\text{T1}} - E^0_{\text{T2}}$ ) and the two different stilbene dianions should be formed in the same potential region:  $E^0_{\text{T2}} - E^0_{\text{C2}} \sim 0.05 \text{ V}$ .

We have started from an  $E^0_{\text{C2}}$  value equal to  $E^0_{\text{C1}} - (E^0_{\text{T1}} - E^0_{\text{T2}})$ , and have attempted to estimate by simulation of the experimental CV (dots in Figures 2) the apparent isomerization rate constants of  $\text{CS}^{2-}$ ,  $k_{i,\text{sim}}$ , for the different electrolytes used. For any electrolyte and with the values of  $k_6$  and  $k_{-6}$  used, it was impossible to find a value of  $k_{i,\text{sim}}$  that allowed a good fit between the simulated and the experimental CVs.

We have found that in order to simulate satisfactorily the cyclic voltammograms,  $E^0_{\text{C1}} - E^0_{\text{C2}}$  had to be smaller than  $E^0_{\text{T1}} - E^0_{\text{T2}}$ . Henceforth, disproportionation of the *cis* isomer of the stilbene anion-radical should be more favored than that of the *trans* isomer, which could indicate that the *cis* isomer of the dianion interacts more strongly with the different cations than the *trans* isomer does.

We have varied  $E^0_{\text{C2}}$  to determine the influence of this parameter on the isomerization rate constant,  $k_{i,\text{sim}}$  whose variations with  $E^0_{\text{C2}}$  for the different electrolytes are reported in Figure 3. For that purpose, the results of the CV simulation obtained in section 4.2.1 were discussed by using a simple analytical model of the isomerization process that took into account only reactions 3–6.

This simple analytical approach lead, when  $\text{CS}^{2-}$  and  $\text{TS}^{2-}$  were supposed at steady-state, to the following expression of the rate of chemical disappearance of  $\text{CS}^{\bullet-}$ :

$$\frac{d[\text{CS}^{\bullet-}]}{dt} = - \frac{k_{i,\text{sim}} K_{\text{disp,CS}} [\text{CS}^{\bullet-}]^2}{\left(1 + \frac{k_{i,\text{sim}} + k_{-5} [\text{TS}^{\bullet-}]}{k_{\text{dif}} [\text{CS}] + k_5 [\text{CS}^{\bullet-}]}\right) [\text{CS}]} = k_{\text{app}} [\text{CS}^{\bullet-}]^2 \quad (11)$$

It is clear from the latter relationship that  $k_{i,\text{sim}}$  is an apparent rate constant that reflects the global isomerization process and not only reaction 4. For a given cation,  $\log k_{i,\text{sim}}$  decreases linearly with  $E^0_{\text{C2}} - E^0_{\text{C1}} - (E^0_{\text{T2}} - E^0_{\text{T1}})$  with a slope close to  $-F/RT \ln 10$ . Since, for a given cation,  $(E^0_{\text{T2}} - E^0_{\text{T1}})$  is constant, that means that  $\log k_{i,\text{sim}}$  increases linearly with the driving force of reaction 3,  $\Delta G^0_3 = E^0_{\text{C1}} - E^0_{\text{C2}}$ . This situation is expected when disproportionation (eq 3) is at equilibrium and the rate-determining step is the dianion isomerization (eq 4) and when  $k_{i,\text{sim}} < k_{\text{dif}} [\text{CS}]$ . Under such circumstances, the apparent rate of disappearance of  $\text{CS}^{\bullet-}$  is given by

$$k_{\text{app}} = k_{i,\text{sim}} K_{\text{disp,CS}} \quad (12)$$

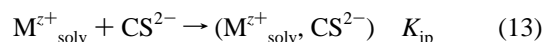
and for a given cation, obtaining a simulated cyclic voltammogram identical to the experimental one implies that  $k_{\text{app}}$  is constant and consequently  $k_{i,\text{sim}} \propto 1/K_{\text{disp,CS}}$  as observed in Figure 3 for each cation.

**4.2.3. Influence of the Nature of the Cation on the Isomerization of the *cis*-Stilbene Dianion.** Cation influence on the kinetics of the cleavage of frangible bonds of anion-radicals has been reported and discussed in terms of ion association.<sup>42</sup> The case of the stilbene isomerization is somehow more complicated since it involves a greater number of reactions that could be cation sensitive.

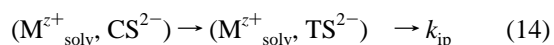
However we have attempted a relevant analysis of cation effects. Several assumptions were then required. To simplify the problem, we have assumed that ion pairing of anion-radicals was negligible compared to association of dianions with cations. We have also postulated that, as observed by simulation of the cyclic voltammograms, the isomerization process was mainly controlled by the isomerization reaction, the disproportionation acting as a preequilibrium and the rate of decay of  $\text{CS}^{\bullet-}$  being given by eq 11.

To go further, if one assumes that  $E^0_{\text{T2}} - E^0_{\text{C2}}$  is independent of the cation, according to Figure 3,  $k_{i,\text{sim}}$  should vary with the nature of the cation and decrease according to the sequence  $\text{Li}^+ \approx \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$ . Under this assumption, simulation of the cyclic voltammograms indicates that the apparent rate constant,  $k_{i,\text{sim}}$ , decreases when going from  $\text{Li}^+ \approx \text{Na}^+$  to  $\text{K}^+$  and  $\text{Mg}^{2+}$ , meanwhile the global disappearance of  $\text{CS}^{\bullet-}$  becomes faster. This could seem odd, at first sight, but comes from the expression of the apparent  $\text{CS}^{\bullet-}$  decay rate constant given by eq 12 and points out the predominant role of disproportionation over isomerization. Indeed, when going from  $\text{Li}^+ \approx \text{Na}^+$  to  $\text{K}^+$  and  $\text{Mg}^{2+}$ ,  $K_{\text{disp,CS}}$  increases much more than  $k_{\text{app}}$  does and consequently  $k_{i,\text{sim}}$  decreases from  $\text{Li}^+ \approx \text{Na}^+$  to  $\text{K}^+$  and  $\text{Mg}^{2+}$ . Those trends reflect the influence of the  $\text{CS}^{2-}$ –cation interaction within the formed ion pair on the isomerization rate. Under this same assumption, one could wonder whether the cation influence can be assigned to ions association thermodynamics or to isomerization kinetics into the ion pair.

If  $K_{\text{ip}}$  corresponds to the *cis*-stilbene dianion association with partly solvated  $\text{M}^{z+}$  cation,



the isomerization process could occur at the level of the free (eq 10) or associated (eq 14) *cis*-stilbene dianion.



where  $k_i$  and  $k_{\text{ip}}$  correspond to the kinetic rate of isomerization of the free and the paired dianion. The global apparent rate

constant for the decay of  $\text{CS}^{\bullet-}$ ,  $k_{\text{app}}$ , now becomes for favored ion association:

$$k_{\text{app}} = (k_i + K_{\text{ip}}[\text{M}^{z+}]k_{\text{ip}}) K_{\text{disp,CS}} \quad (15)$$

A similar expression relates the standard reduction potential of the free,  $E_{\text{C2,0}}^0$ , and paired,  $E_{\text{C2,ip}}^0$ , *cis* isomer dianion and  $K_{\text{ip}}$ :

$$E_{\text{C2,ip}}^0 = E_{\text{C2,0}}^0 + \frac{RT}{F} \ln(1 + K_{\text{ip}}[\text{M}^{z+}]) \quad (16)$$

This equation indicates that the dianion association favors the disproportionation reaction, and consequently,  $K_{\text{ip}}[\text{M}^{z+}] = K_{\text{disp,CS,M}}/K_{\text{disp,CS}}$ , where  $K_{\text{disp,CS,M}}$  and  $K_{\text{disp,CS}}$  are, respectively, the disproportionation constant for the paired (with cation  $\text{M}^{z+}$ ) and free  $\text{CS}^{2-}$ . Equation 15 can be rewritten as a function of the variable  $K_{\text{disp,CS,M}}$ , which is available from the simulations:

$$k_{\text{app}} = (k_i/K_{\text{ip}}[\text{M}^{z+}] + k_{\text{ip}}) K_{\text{disp,CS,M}} = (k_i K_{\text{disp,CS}}/K_{\text{disp,CS,M}} + k_{\text{ip}}) K_{\text{disp,CS,M}} \quad (20)$$

From this simple treatment, one would predict, for a process governed by the isomerization within, respectively, the free species and the paired ones, that  $k_{\text{app}}$  is a constant or varies according to  $k_{\text{ip}}K_{\text{disp,CS,M}}$ , respectively, when changing the nature of the cation. This would mean that the value of the isomerization rate constant obtained from simulation of the cyclic voltammograms,  $k_{\text{isim}}$ , is proportional to  $1/K_{\text{disp,CS,M}}$  or to  $k_{\text{ip}}$ , respectively, for free or ion-paired dianion mechanism. When changing the cation of the electrolyte, and for any constant value of  $E_{\text{T2}}^0 - E_{\text{C2}}^0$ , we observe that,  $k_{\text{isim}}$  is somewhat proportional to  $1/K_{\text{disp,TS,M}}^{0.4}$  (when  $E_{\text{T2}}^0 - E_{\text{C2}}^0$  is kept constant,  $K_{\text{disp,CS,M}}$  is proportional to  $K_{\text{disp,TS,M}}$ ).

This result would be more likely in favor of a kinetic control by the isomerization within the ion-paired dianionic species. It seems difficult to go further in the analysis, but anyway a conclusion can be drawn from that model: as disproportionation becomes more favored than the decay of  $\text{CS}^{\bullet-}$ , isomerization of  $\text{CS}^{2-}$  gets slower when going from  $\text{Li}^+ \approx \text{Na}^+$  to  $\text{K}^+$  and  $\text{Mg}^{2+}$ , which means that when increasing the association between the cation and  $\text{CS}^{2-}$ , the isomerization within the ion pair gets slower. It is in agreement with the trends found in less dissociating solvents (such as THF) and indicates that the closer the cation and  $\text{CS}^{2-}$ , the slower the rotation around the C—C bond.<sup>22–25</sup> If  $E_{\text{T2}}^0 - E_{\text{C2}}^0$  changes with the nature of the cation, the situation becomes too intricate for any conclusion to be drawn.

## 5. Conclusion

We have investigated the reductive isomerization of *cis*-stilbene in liquid ammonia at  $-40^\circ\text{C}$  in the presence of various cations. We have observed on the cyclic voltammograms that isomerization was favored when going from  $\text{Li}^+ \approx \text{Na}^+$  to  $\text{K}^+$  and  $\text{Mg}^{2+}$ , which proved that the isomerization proceeded at the level of the dianion since dianions are the most sensitive to cations in liquid ammonia. From the changes in the standard reduction potential of the anion-radical, the cation should be associated with a dianion in an ion-pair structure in which the ions may keep their solvation shell.

Proper simulation of the cyclic voltammograms implied that *cis*-stilbene anion-radical disproportionation was much more efficient than that of the *trans* one. Simulation showed that the isomerization process was mainly governed by the isomerization reaction, the disproportionation reaction acting as a preequilib-

rium. Specific effects of the cations were more difficult to rationalize since the reaction scheme involved a great number of cation-sensitive reactions. However, we have interpreted the observation that the global isomerization process was favored when going from  $\text{Li}^+ \approx \text{Na}^+$  to  $\text{K}^+$  and  $\text{Mg}^{2+}$  by a simple model involving rough approximations and only association within dianionic species. This model pointed out the predominant effect of disproportionation over isomerization: when going from  $\text{Li}^+ \approx \text{Na}^+$  to  $\text{K}^+$  and  $\text{Mg}^{2+}$ , disproportionation got favored and isomerization on the elemental step disfavored. Consequently the isomerization of  $\text{CS}^{2-}$  was supposed to proceed within the ion pair and the stronger the interaction between the cation and the dianion, the slower the rotation around the C—C bond.

## References and Notes

- Geraldo, M. D.; Montenegro, M. I.; Slevin, L. *J. Phys. Chem. B* **2001**, *105*, 3182.
- Wawzonek, S.; Blaha, E. W.; Berkey, R.; Runner, M. E. *J. Electrochem. Soc.* **1955**, *102*, 235.
- Grodzka, P. G.; Elving, P. J. *J. Electrochem. Soc.* **1963**, *110*, 231.
- Grzeszczuk, M.; Smith, D. E. *J. Electroanal. Chem.* **1984**, *162*, 189.
- Dietz, R.; Peover, M. E. *Discuss. Faraday Soc.* **1968**, 154.
- Funt, B. L.; Gray, D. G. *J. Electrochem. Soc.* **1970**, *117*, 1020.
- Troll, T.; Baizer, M. M. *Electrochim. Acta* **1974**, *19*, 951.
- Farnia, G.; Maran, F.; Sandonà, G. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1885.
- Schultz, D. A.; Fox, M. A. *J. Org. Chem.* **1990**, *55*, 1047.
- Muzyka, J. L.; Fox, M. A. *J. Org. Chem.* **1991**, *56*, 4549.
- Wolf, M. O.; Fox, H. H.; Fox, M. A. *J. Org. Chem.* **1996**, *61*, 287.
- Wawzonek, S.; Wearing, D. *J. Am. Chem. Soc.* **1959**, *81*, 2067.
- Ammar, F.; Savéant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, *47*, 115.
- Parker, V. D.; Nyberg, K.; Ebersson, L. *J. Electroanal. Chem.* **1969**, *22*, 150.
- Roberts, R. C.; Szwarc, M. *J. Am. Chem. Soc.* **1965**, *94*, 5542.
- Cserhegyi, A.; Jagur-Grodzinski, J.; Szwarc, M. *J. Am. Chem. Soc.* **1969**, *91*, 1892.
- Lundgren, B.; Levin, G.; Claesson, S.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, *97*, 262.
- DeGroof, B.; Levin, G.; Szwarc, M. *J. Am. Chem. Soc.* **1977**, *99*, 474.
- Levin, G.; Claesson, S.; Szwarc, M. *J. Am. Chem. Soc.* **1972**, *94*, 8672.
- Hojtink, G. J.; van der Meij, P. H. Z. *Phys. Chem. (Frankfurt am Main)* **1959**, *20*, 1.
- Waack, R.; Doran, M. A. *J. Organomet. Chem.* **1965**, *3*, 92.
- Levin, G.; Ward, T. A.; Szwarc, M. *J. Am. Chem. Soc.* **1974**, *96*, 270.
- Ward, T. A.; Levin, G.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, *97*, 258.
- Sorensen, S.; Levin, G.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, *97*, 2341.
- Wang, H. C.; Levin, G.; Szwarc, M. *J. Am. Chem. Soc.* **1977**, *99*, 2642.
- Jensen, B. S.; Lines, R.; Pagsberg, P.; Parker, V. D. *Acta Chem. Scand. B* **1977**, *31*, 707.
- Nozaki, K.; Naito, A.; Ho, T.-I.; Hatano, H.; Okazaki, S. *J. Phys. Chem.* **1989**, *93*, 8304.
- Levin, G.; Szwarc, M. *Chem. Phys. Lett.* **1975**, *35*, 323.
- Chang, R.; Markgraf, J. H. *Chem. Phys. Lett.* **1972**, *13*, 575.
- Baik, M.-H.; Schauer, C. K.; Ziegler, T. *J. Am. Chem. Soc.* **2002**, *124*, 11167.
- Combellas, C.; Kanoufi, F.; Thiébaud, A. *J. Electroanal. Chem.* **2001**, *499*, 144.
- Herlem, M. *Bull. Soc. Chim. Fr.* **1967**, 1687.
- (a) Thiébaud, A. 19th Sandbjerg Meeting 1996, Sandbjerg, 14/6–16/6 **1996**. (b) Thiébaud, A. *Journées d'Electrochimie* 1997, Montréal, 30/6–5/7 **1997**.
- Demortier, A.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 3495.
- Smentowski, F. J.; Stevenson, G. R. *J. Am. Chem. Soc.* **1968**, *90*, 4461.
- Thompson, J. C. In *The Chemistry of Non-Aqueous Solvents*, Vol. II: Acidic and Basic Solvents; Lagowski, J. J., Ed.; Academic Press: New York, 1967; pp 265–317.
- Gill, J. B. In *The Chemistry of Non-Aqueous Solutions, Current Progress*; Mamantov, G.; Popov, A. I., Eds.; VCH: New York, 1994; pp 149–178.

(38) Amatore, C.; Pinson, J.; Savéant, J.-M.; Thiébaud, A. *J. Electroanal. Chem.* **1981**, 103, 6930.

(39) Riddick, J. A.; Bunger, W. B. In *Techniques of Chemistry*, Vol. 2, Organic solvent; Physical properties and methods of purification, 3rd ed.; Wiley Interscience, New York, 1972; p 446.

(40) Szwarc, M. In *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley: New York, 1974; Vol. 2, pp 1–150.

(41) Nadjó, L.; Savéant, J.-M. *J. Electroanal. Chem.* **1973**, 48, 113.

(42) Andrieux, C. P.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1995**, 117, 9340.