

A typical example treated by this procedure is the reaction of methyl vinyl ketone with ethyl acetoacetate in water. Table I lists the initial conditions and the experimental data obtained. Equation 3 represents

$$\begin{aligned}
 [\text{MVK}] = & 0.36860 - (3.1727 \times 10^{-3}t) + \\
 & (1.94173 \times 10^{-5}t^2) - (8.23999 \times 10^{-8}t^3) + \\
 & (2.33115 \times 10^{-10}t^4) - (4.35564 \times 10^{-13}t^5) + \\
 & (5.29537 \times 10^{-16}t^6) - (4.02167 \times 10^{-19}t^7) + \\
 & (1.73052 \times 10^{-22}t^8) - (3.21784 \times 10^{-26}t^9) \quad (3)
 \end{aligned}$$

the experimentally determined concentrations expressed as a function of time. This equation, together with the initial concentration of ethyl acetoacetate and the previously determined first-order decomposition constant,  $k_1$ , were incorporated into a computer program which subjected these data to the foregoing procedure.

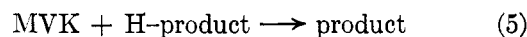
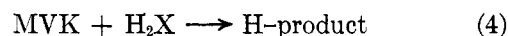
Table II: Typical Values of  $k_1$

Time, sec	$k_1$ , $M^{-1} \text{ sec}^{-1}$	Time, sec	$k_1$ , $M^{-1} \text{ sec}^{-1}$
100	0.03619	405	0.03597
101	0.03587	406	0.03595
102	0.03608	407	0.03595
103	0.03513	408	0.03591
104	0.03629	409	0.03589
105	0.03601		
106	0.03533	600	0.03543
107	0.03598	601	0.03565
108	0.03587	602	0.03560
109	0.03514	603	0.03550
		604	0.03513
200	0.03455	605	0.03557
201	0.03521	606	0.03547
202	0.03469	607	0.03583
203	0.03508	608	0.03561
204	0.03495	609	0.03597
205	0.03569		
206	0.03429	800	0.03610
207	0.03557	801	0.03608
208	0.03535	802	0.03591
209	0.03510	803	0.03602
		804	0.03600
400	0.03601	805	0.03642
401	0.03607	806	0.03594
402	0.03601	807	0.03585
403	0.03599	808	0.03608
404	0.03622	809	0.03610

Typical values of  $k_2$  for the experiment presented are shown in Table II.

A similar technique was employed for Michael reactions in which the donor molecule, bearing two  $\alpha$ -

hydrogens, was capable of attacking two methyl vinyl ketone molecules in two successive steps



Therefore

$$\begin{aligned}
 -\delta[\text{MVK}]/\delta t = & k_1[\text{MVK}][\text{H}_2\text{X}] + \\
 & k_2[\text{MVK}][\text{H-product}] \quad (6)
 \end{aligned}$$

where  $k_1$  was determined for dilute, weakly basic systems. This general technique appears to be applicable to other types of systems of concurrent reactions, but a lack of suitable experimental data at this time prevents its explicit and immediate application.

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## The Structure of the Iodine-Triphenylamine Charge-Transfer Complex

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Stamires and Turkevich,<sup>1</sup> in a study of paramagnetic charge-transfer complexes, reported obtaining a five-line epr spectrum from a solution of triphenylamine (TPA) and iodine in various solvents. This spectrum was attributed to a bimolecular TPA radical ion  $[(\text{C}_6\text{H}_5)_3\ddot{\text{N}}\dot{\text{N}}(\text{C}_6\text{H}_5)_3]^+$ . Recent electrochemical studies<sup>2</sup> in one of these laboratories indicated that the cation radical of N,N,N',N'-tetraphenylbenzidine is probably responsible for the five-line spectrum obtained by Stamires and Turkevich. This note summarizes further proof of this assignment.

The anodic oxidation of TPA in various nonaqueous solvents has been shown to proceed *via* formation of the

(1) D. N. Stamires and J. Turkevich, *J. Am. Chem. Soc.*, **85**, 2557 (1963).

(2) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *ibid.*, **88**, 3498 (1966).

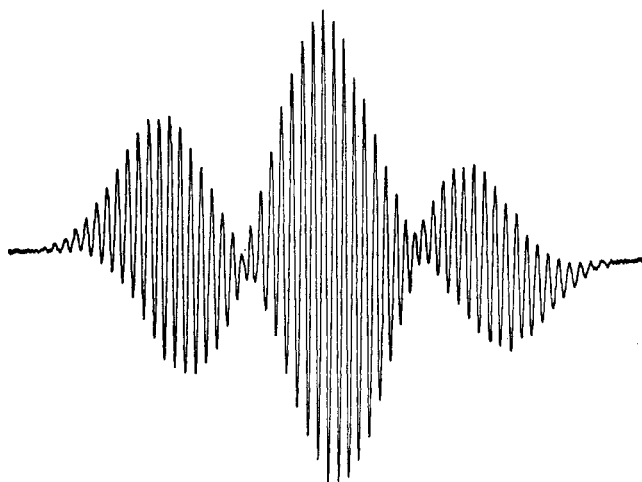
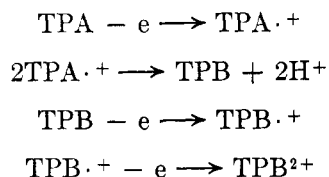


Figure 1. Epr spectrum from addition of iodine to trianisylamine.

triarylamine cation radical  $\text{TPA}^{\cdot+}$ . This has only a transient existence and couples rapidly to give the corresponding substituted  $\text{N,N,N',N'}$ -tetraphenylbenzidine (TPB). The TPB is oxidizable at or near the same potential and it immediately becomes further oxidized. Although the benzidine can be fully oxidized to the diquinoid form, its cation radical  $\text{TPB}^{\cdot+}$  is quite stable and it is this radical ion species which accumulates in solution oxidation of TPA. The reactions are summarized as



The oxidation of *para*-substituted triphenylamines like tri-*p*-anisylamine (TAA), tri-*p*-tolylamine (TTA), and *N*-methyl-di-*p*-anisylamine (MDAA) results, however, in the corresponding stable substituted triarylamine cation radical. The difference between the behavior of these compounds and TPA is clearly the inability of the cation radicals of TAA, TTA, and MDAA to couple and form *p*-benzidines. The resolved and interpreted epr spectra of the cation radicals of TAA, TTA, and MDAA obtained from electrolyzed solutions have been reported.<sup>2</sup> The electrolysis of TPA yields a five-line spectrum which is identical with that obtained from an electrolyzed solution of authentic  $\text{N,N,N',N'}$ -tetraphenylbenzidine.

The iodine-triarylamine interaction appears to duplicate the electrochemical oxidation pathways for the above mentioned amines. Although the results are identical in the solvents methylene chloride, di-

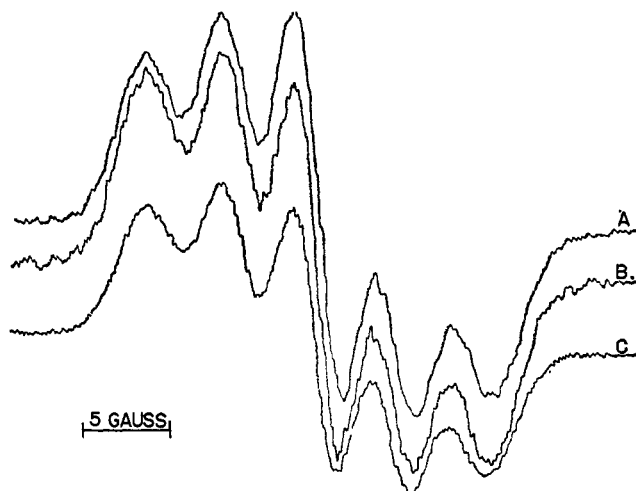


Figure 2. Comparison of the epr spectra of oxidized triphenylamine and  $\text{N,N,N',N'}$ -tetraphenylbenzidine: A, spectrum from interaction of iodine and triphenylamine; B, spectrum from electrochemical oxidation of tetraphenylbenzidine; C, spectrum from interaction of iodine and tetraphenylbenzidine.

methoxyethane, and acetonitrile, the best resolution of the epr spectra was obtained in propylene carbonate (PC).

Figure 1 shows the spectrum obtained from the addition of iodine to a *ca.*  $10^{-3} M$  solution of TAA. The spectrum is unequivocal and has been interpreted as corresponding to the cation radical of the parent molecule.<sup>2,3</sup> The splittings are identical with those obtained by electrooxidation of TAA in acetonitrile.<sup>2</sup> (The unequal intensities have also been observed by Walter.<sup>3</sup>) Similar results were obtained for MDAA and TTA in PC. In each of these cases, *with all para positions blocked, the addition of iodine produced the spectrum of the simple cation radical of the parent amine.* This is consistent with a simple chemical oxidation identical with the electrochemical pathway.

When triphenylamine and iodine are mixed in PC, a broad five-line spectrum results (Figure 2A). This spectrum compares favorably with that obtained from an iodine-tetraphenylbenzidine solution (Figure 2C). Furthermore, this same five-line resonance is exhibited when tetraphenylbenzidine is electrochemically oxidized in PC (Figure 2B). Some hyperfine structure was obtained in all three cases. The epr spectrum of the cation radical of TPB has not been totally interpreted, thus these data are not unequivocal. However, beyond reasonable doubt, the three epr spectra belong to the same paramagnetic species  $\text{TPB}^{\cdot+}$ . Similar results were found for the following partially substituted tri-

(3) R. I. Walter, *J. Am. Chem. Soc.*, **88**, 1923 (1966).

phenylamines and their corresponding benzidines: 4-methyltriphenylamine, 4-nitrotriphenylamine, 4-methoxytriphenylamine, tri-*o*-anisylamine, and tri-*o*-tolylamine.<sup>4</sup>

In general, it can be concluded that, if the triphenylamine has open *para* positions, coupling of the primary radical ions will occur and the N,N,N',N'-substituted benzidine cation radicals will be observed. The present results are in accord with the recent report of Norman, *et al.*,<sup>5</sup> that chemical oxidation of TPA by lead tetracetate-boron trifluoride leads to TPB<sup>•+</sup>. Clearly the spectrum reported by Stamires and Turkevich<sup>1</sup> was that of the cation radical of the coupling product TPB.

The equilibrium constant for the oxidation of TPA by iodine as calculated from the experimental redox potentials is *ca.*  $5 \times 10^{-5}$ . The over-all reaction is somewhat favored by the fact that TPB is more easily oxidized than TPA. The solutions were clearly in equilibrium, as the addition of iodine to solutions containing some excess iodine always brought about an increase in epr signal. In the case of 4-nitrotriphenylamine, much lower radical concentrations were noted at corresponding iodine concentration. This is consistent with the higher observed oxidation potential of this compound.

From the above, it can be seen that in certain cases the distinction between charge-transfer complex formation and simple oxidation-reduction reactions becomes largely academic. As a consequence, the study of these complexes may sometimes be complicated by follow-up reactions very similar to those encountered in organic electrochemistry.

**Acknowledgment.** This work was supported by the National Science Foundation through Grant GP-5079X, and this support is gratefully acknowledged.

(4) W. H. Bruning, unpublished data.

(5) D. L. Allara, B. C. Gilbert, and R. O. C. Norman, *Chem. Commun.*, 319 (1965).

### Effect of Similions on the Coagulation of Silver Bromide Sols in *Statu Nascendi*

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The Schulze-Hardy rule states that the flocculation value for an ion whose charge is the opposite of that

**Table I:** The Critical Coagulation Concentration<sup>a</sup> of Cations for a Negative Silver Bromide Sol

Coagulating electrolyte	Ccc, <sup>a</sup> equiv/l.
Univalent	
LiNO <sub>3</sub>	0.102
$\frac{1}{2}$ Li <sub>2</sub> SO <sub>4</sub>	0.137
NaNO <sub>3</sub>	0.080
$\frac{1}{2}$ Na <sub>2</sub> SO <sub>4</sub>	0.109
KNO <sub>3</sub>	0.058
$\frac{1}{2}$ K <sub>2</sub> SO <sub>4</sub>	0.078
$\frac{1}{2}$ Rb <sub>2</sub> SO <sub>4</sub>	0.058
CsNO <sub>3</sub>	0.035
$\frac{1}{2}$ Cs <sub>2</sub> SO <sub>4</sub>	0.042
Divalent	
Mg(NO <sub>3</sub> ) <sub>2</sub>	$4.2 \times 10^{-3}$
Mn(NO <sub>3</sub> ) <sub>2</sub>	$3.5 \times 10^{-3}$
Ca(NO <sub>3</sub> ) <sub>2</sub>	$3.4 \times 10^{-3}$
Sr(NO <sub>3</sub> ) <sub>2</sub>	$3.1 \times 10^{-3}$
Ba(NO <sub>3</sub> ) <sub>2</sub>	$3.1 \times 10^{-3}$
Trivalent	
Ce(NO <sub>3</sub> ) <sub>3</sub>	$7.8 \times 10^{-5}$
La(NO <sub>3</sub> ) <sub>3</sub>	$7.9 \times 10^{-5}$
Al(NO <sub>3</sub> ) <sub>3</sub>	$9.4 \times 10^{-5}$
Tetravalent	
Zr(NO <sub>3</sub> ) <sub>4</sub>	$3.9 \times 10^{-6}$
Th(NO <sub>3</sub> ) <sub>4</sub>	$3.9 \times 10^{-6}$

<sup>a</sup> Values of ccc are taken from plots in ref 3.

of the sol increases with the ionic charge. The theory of Verwey and Overbeek<sup>1</sup> predicts that the ratios of these concentrations should be as the inverse sixth power of the valences

$$C_{\text{uni}}:C_{\text{di}}:C_{\text{tri}}:\dots = 1^{-6}:2^{-6}:3^{-6}:\dots \quad (1)$$

Težak, Matijević, and co-workers<sup>2</sup> have made extensive studies of the coagulation-by-electrolytes process. Some of their results are summarized in Table I.<sup>3</sup> The large change in the critical coagulation concentration (ccc) with counterion charge is seen in the data. The small differences in values for alkali metal nitrates and sulfates shows that the ccc is somewhat dependent upon the nature of the similion.

While it is known that the effect of similions on colloid coagulation by counterions is small, very little

(1) E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier Publishing Co., New York, N. Y., 1948.

(2) References to prior work can be found in the following: (a) B. Cerniki and B. Težak, *Croat. Chem. Acta*, **29**, 7 (1957); (b) S. Kratochvil, B. Težak, and J. P. Kratochvil, *J. Colloid Sci.*, **19**, 373 (1964); (c) E. Matijević, M. Abramson, R. Ottewill, K. Schulz, and M. Kerker, *J. Phys. Chem.*, **65**, 1724 (1961).

(3) B. Težak, E. Matijević, and K. Schulz, *ibid.*, **59**, 769 (1955).