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# Effect of External Pressure on Photoinduced Electron-Transfer Reactions in the Marcus Inverted Region

Wen-Sheng Chung, Nicholas J. Turro,\*

Department of Chemistry, Columbia University, New York, New York 10027

Ian R. Gould,\* and Samir Farid\*

Corporate Research Laboratories, Eastman Kodak Company, Rochester, New York 14650-2109

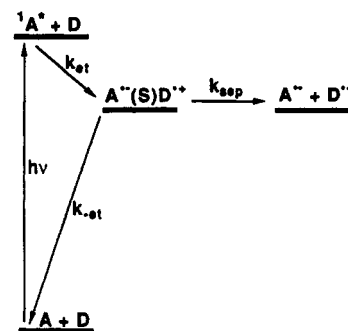
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The effect of pressure on the quantum yields for formation of free-radical ions ( $\Phi_{\text{ions}}$ ) in the photoinduced bimolecular electron-transfer reactions of the excited-state acceptors 9,10-dicyanoanthracene (DCA), 2,6,9,10-tetracyanoanthracene (TCA), and *N*-methylacridinium ( $\text{MA}^+$ ), with simple alkyl-substituted benzene donors, has been studied in acetonitrile at room temperature. The values of  $\Phi_{\text{ions}}$ , which are determined by the competition between return electron transfer ( $k_{\text{et}}$ ) and separation ( $k_{\text{sep}}$ ) within the initially formed geminate radical ion pairs, are found to decrease with increasing pressure. The results are discussed in terms of the pressure effects on the individual rate constants  $k_{\text{et}}$  and  $k_{\text{sep}}$ . The  $k_{\text{et}}$  process is unique among those electron-transfer reactions whose pressure dependence has been studied since the reactions are in the Marcus "inverted" region and are nonadiabatic. Measurements of the relative rates of electron transfer as a function of reaction exothermicity allow the effect of pressure on the reorganization energy to be determined. Simple dielectric continuum models predict that the solvent reorganization energy should significantly decrease with applied pressure due to changes in the solvent dielectric constant and refractive index, whereas small increases are observed. Possible reasons for this discrepancy are discussed. Electron transfer from a neutral donor to DCA or TCA forms a radical anion/radical cation pair, whereas electron transfer to  $\text{MA}^+$  forms a radical/radical cation pair. Different pressure dependencies are observed for  $\Phi_{\text{ions}}$  when the cyanoanthracene and  $\text{MA}^+$  acceptors are used which are attributed to differing influences of electrostriction on  $k_{\text{et}}$  for the two acceptors.

## Introduction

Photoinduced electron transfer to form radical ions is now well established as an important mechanism for product formation in organic photochemistry.<sup>1</sup> The overall quantum yields of these reactions, however, vary over a wide range.<sup>1-3</sup> This can be understood with reference to Scheme I, which summarizes the simplest mechanism for the formation of radical ions in a polar solvent such as acetonitrile. Electron transfer occurs upon diffusional encounter between, in this case, an excited acceptor ( $^1\text{A}^*$ ) and a donor (D), to form a solvent-separated geminate radical-ion pair ( $\text{A}^{\cdot-}(\text{S})\text{D}^{\cdot+}$ , center-to-center distance ca. 6–8 Å). The radical-ion pairs undergo return electron transfer to re-form the starting materials ( $\text{A} + \text{D}$ ,  $k_{\text{et}}$ ), in competition with separation to form the radical ions in solution ( $\text{A}^{\cdot-} + \text{D}^{\cdot+}$ ,  $k_{\text{sep}}$ ). Chemical product formation can compete with return electron transfer and separation within the geminate radical ion pair in very few cases,<sup>2</sup> and products usually arise from reactions of the separated radical ions.<sup>1</sup> Therefore, in the absence of chain processes, the yields of formation of the separated radical ions,  $\Phi_{\text{ions}}$ , determine the limiting quantum yields for product formation,<sup>1c,3</sup> and the return electron-transfer step thus represents the primary energy-wasting process in these reactions. It has now been clearly established by several groups<sup>3-8</sup> that the rates of return electron transfer within

## SCHEME I



geminate radical-ion pairs follow the general predictions of Marcus electron-transfer theory.<sup>9</sup> An interesting consequence of the Marcus theory behavior is that, since the return electron-transfer reactions are usually quite exothermic (typically by ca. 1–3 eV), the reactions are often in the "inverted" region, and a decrease in reaction rate with increasing reaction exothermicity is observed.<sup>3-8</sup> The inverted region effect has a profound influence on the overall efficiencies of photoinduced bimolecular electron-transfer reactions.<sup>3</sup> Ion pairs for which the return electron transfer is very exothermic (high-energy ion pairs) undergo slow energy wasting return electron transfer, which results in efficient formation of separated radical ions in solution, whereas low-energy radical ion pairs undergo rapid energy-wasting return electron transfer which results in the formation of separated radical ions with low efficiency.<sup>3</sup> The radical-ion-pair systems provide one of the clearest examples of the inverted region, and in fact have proven to be convenient model systems for the study of many aspects of electron-transfer kinetics, including the effects of isotopic substitution<sup>10a</sup> and molecular dimension.<sup>10b</sup>

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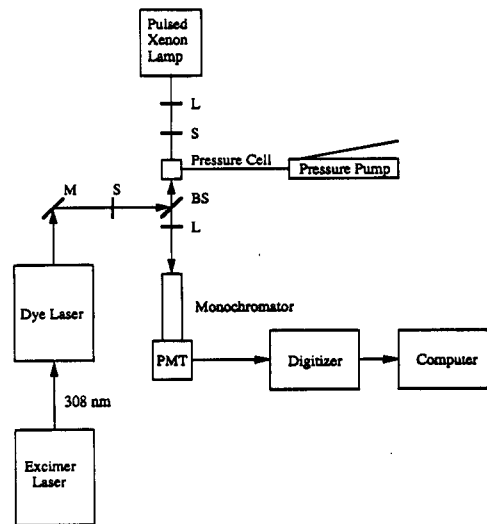
**TABLE I: Pressure Dependence of the Quantum Yields for Formation of Separated Radical Ions from Cyanoanthracene Radical Anion/Alkylbenzene Radical Cation Pairs in Acetonitrile at 25 °C**

| donor                      | acceptor | $\Delta G_{\text{et}}$ , eV | $\Delta V^*(\Phi_{\text{sep}})$ , cm <sup>3</sup> mol <sup>-1</sup> | $\Delta V^*(k_{\text{et}}/k_{\text{sep}})$ , cm <sup>3</sup> mol <sup>-1</sup> |
|----------------------------|----------|-----------------------------|---|--|
| 1,2,4-trimethylbenzene     | DCA      | -2.83                       | +6.8  | -9.3   |
| 1,2,3,4-tetramethylbenzene | DCA      | -2.75                       | +6.5  | -8.2   |
| durene                     | DCA      | -2.69                       | +6.7  | -8.1   |
| pentamethylbenzene         | DCA      | -2.62                       | +9.6  | -10.6  |
| m-xylene                   | TCA      | -2.58                       | +7.7  | -8.4   |
| mesitylene                 | TCA      | -2.55                       | +7.8  | -8.2   |
| p-xylene                   | TCA      | -2.50                       | +7.6  | -8.1   |
| 1,2,4-trimethylbenzene     | TCA      | -2.36                       | +6.9  | -7.1   |
| 1,2,3,4-tetramethylbenzene | TCA      | -2.28                       | +7.3  | -7.4   |
| durene                     | TCA      | -2.22                       | +7.4  | -7.7   |

Although pressure has long been known to be a useful tool in the elucidation of reaction mechanisms,<sup>11</sup> very little work has been published concerning the effects of high pressure on photochemical processes,<sup>12</sup> particularly for photoinduced electron-transfer reactions.<sup>13</sup> Most of the reported examples of pressure effects on photoinduced electron-transfer reactions have been concerned with intermolecular quenching of excited-state transition-metal complexes.<sup>13</sup> Such intermolecular electron-transfer reactions, however, are often complicated by the influence of diffusional processes, and indeed, in such systems it is not possible to determine absolute rates of electron transfer when the reactions become diffusion controlled.<sup>14</sup> Electron self-exchange reactions provide a more direct measure of electron-transfer rates, and several studies of the effects of pressure on the rates of these processes in inorganic systems have been published,<sup>15</sup> although these reactions can also be complicated by ionic strength effects.<sup>15c</sup> It is clear that the influence of external pressure on the efficiencies of bimolecular photoinduced organic electron-transfer chemical reactions cannot be easily predicted. The return electron-transfer reactions in radical-ion pairs represent an interesting system for the study of pressure effects because the reactions are first order and thus are not complicated by the requirement that the donor and acceptor diffuse together before electron transfer can take place.<sup>3</sup> Furthermore, whereas the self-exchange reactions which have been studied previously are examples of electron-transfer reactions in the Marcus normal region, and are probably adiabatic, the return electron-transfer reactions  $k_{\text{et}}$  represent good examples of reactions in the inverted region and are therefore nonadiabatic.<sup>9b</sup> Finally, by definition it is not possible to study the effect of reaction free energy in self-electron-exchange reactions ( $\Delta G_{\text{et}} = 0$ ), whereas in the geminate ion-pair systems the driving force can be varied over a wide range, and thus information concerning changes in

**TABLE II: Pressure Dependence of the Quantum Yields for Formation of Separated Radical Ions from Methylacridine Radical/Alkylbenzene Radical Cation Pairs in Acetonitrile at 25 °C**

| donor                  | $\Delta G_{\text{et}}$ , eV | $\Delta V^*(\Phi_{\text{sep}})$ , cm <sup>3</sup> mol <sup>-1</sup> | $\Delta V^*(k_{\text{et}}/k_{\text{sep}})$ , cm <sup>3</sup> mol <sup>-1</sup> |
|------------------------|-----------------------------|---|--|
| m-xylene               | -2.59                       | +9.0  | -11.0  |
| mesitylene             | -2.56                       | +10.3   | -11.6  |
| p-xylene               | -2.51                       | +11.0   | -12.2  |
| 1,2,4-trimethylbenzene | -2.37                       | +9.5  | -10.0  |
| durene                 | -2.23                       | +9.2  | -9.6   |



**Figure 1.** Schematic representation of the high-pressure transient absorption spectrometer: BS, beam splitter; L, lens; M, mirror; and S, shutter.

the reorganization parameters can in principle be obtained.

In this paper we describe the results of a study in which the effects of external pressure on the dynamics of several geminate radical-ion pairs were investigated. The experiments involve the measurement of the quantum yields for formation of separated radical ions from the geminate radical-ion pairs ( $\Phi_{\text{ions}}$ ) in acetonitrile at room temperature, using a transient absorption technique described previously.<sup>3</sup> As described above, the quantum yields are determined by the competition between return electron transfer,  $k_{\text{et}}$ , and ion pair separation,  $k_{\text{sep}}$  (Scheme I). In order to investigate the influence of electrostriction effects on the separated radical-ion yield, experiments were performed using ground-state neutral acceptors with neutral donors, in which case radical anion/radical cation pairs are formed, and compared to those using a ground-state cationic acceptor, in which case neutral radical/radical cation pairs are formed.

## Experimental Section

Experiments were performed in argon-purged acetonitrile using 9,10-dicyanoanthracene (DCA), 2,6,9,10-tetracyanoanthracene (TCA), and *N*-methylacridinium hexafluorophosphate ( $\text{MA}^+$ ) as the excited-state sensitizers and electron acceptors, and the simple alkyl-substituted benzenes summarized in Tables I and II as the electron donors. The materials used were the same as those described previously.<sup>3,16</sup> The high-pressure cell has also been described previously.<sup>12e</sup> A circulating water supply maintained the sample chamber at  $25.0 \pm 0.5$  °C during all measurements.

The laser flash photolysis apparatus is similar to that used in previous experiments,<sup>12c</sup> and is shown schematically in Figure 1. For excitation an excimer laser-pumped dye laser at 410 and 402 nm (DPS (Exciton), ca. 15 ns) was used. The energy of the dye laser pulse was always less than 1 mJ/per pulse. The probe light beam (from a pulsed xenon arc lamp) and the exciting laser beam irradiated the sample collinearly in the high-pressure cell. The transmitted light intensity was detected after passing through a

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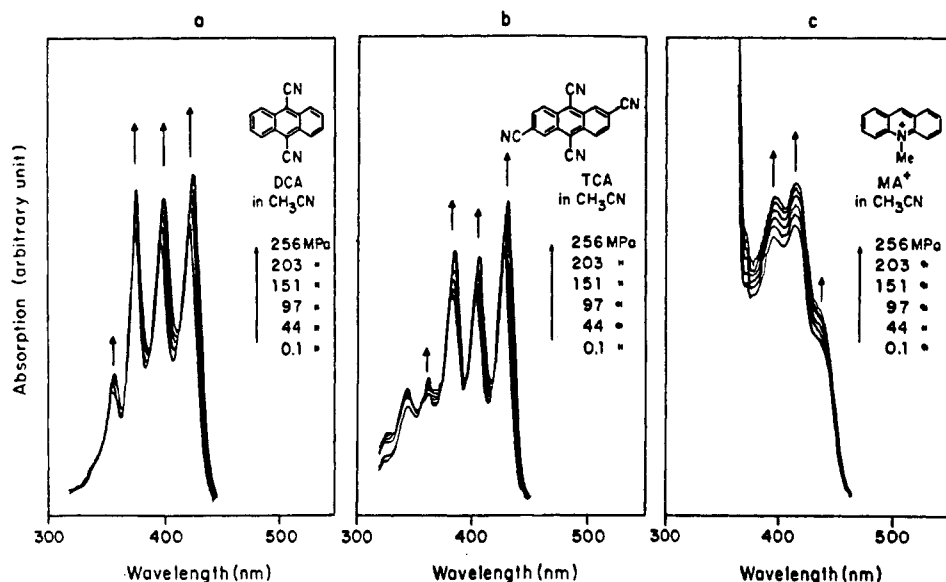
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**Figure 2.** UV/visible absorption spectra of the sensitizers (a) DCA, (b) TCA, and (c)  $\text{MA}^+$  in acetonitrile as a function of pressure at 25 °C.

monochromator (ISA H10) using six dynodes of an RCA 4840 photomultiplier tube terminated in 50  $\Omega$ . The photomultiplier tube output was monitored with a Tektronix 7912-AD waveform digitizer. Normally 10 measurements were taken at each pressure, each measurement being an average of four runs. All data were analyzed on a PDP 11/23 computer which was interfaced to the digitizer.

The quantum yields for formation of separated radical ions from the initially formed geminate radical-ion pairs ( $\Phi_{\text{ions}}$ ) were measured by scavenging the separated radical cations using 4,4'-dimethoxystilbene (DMS), as described previously.<sup>3</sup> The concentration of the DMS ( $5 \times 10^{-4}$  M) was sufficient to scavenge all of the separated radical cations over the entire pressure range, but low enough so that interception of the excited state of the acceptor was negligible compared to the alkylbenzene donor. The donor concentrations ranged between 0.1 and 0.5 M. The experiments involved measuring the transient absorption due to the DMS radical cation formed in the scavenging reaction, as a function of pressure for each donor/acceptor pair. The changes in transient absorption were taken to be directly proportional to the changes in  $\Phi_{\text{ions}}$ . In independent experiments it was shown that the absorption maximum and band shape of the DMS radical cation in acetonitrile did not change significantly over the range of the applied pressure.

The concentrations of the DCA, TCA, and  $\text{MA}^+$  were adjusted so that the solutions had absorbances of ca. 0.5–0.7 at the laser excitation wavelength, which for most experiments was 410 nm. Some experiments were also performed using excitation at 402 nm for systems in which TCA was the sensitizer because of the large pressure dependence of the solution optical densities at 410 nm in these cases (a 64% increase in optical density was observed at 256 MPa; Figure 2). The observed quantum yields were corrected for the small changes (ca. 10%) in the optical densities of the solutions at the excitation wavelengths (Figure 2). In the pressure cell only relative quantum yields were measured. The quantum yields at atmospheric pressure were taken from previous work.<sup>3,16</sup> Steady-state fluorescence measurements were performed to confirm that the concentrations of the donors employed were sufficient to quench more than 95% of the fluorescence of the excited-state acceptors at all of the pressures studied. The ion yields were corrected for changes in the fluorescence quenching efficiencies with increasing pressure.

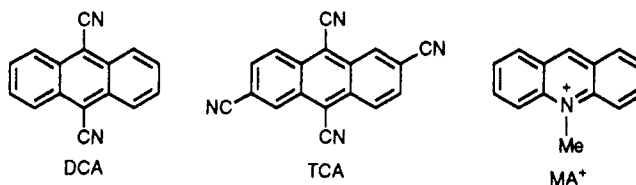
Linear least-squares analysis was used to obtain the volumes of activation as shown in eq 1, in which  $\Phi_P$  represents the ex-

$$(\partial \ln \Phi_P / \partial P)_T = -\Delta V^\ddagger / RT \quad (1)$$

perimental quantum yield at pressure  $P$ . The errors in the activation volumes are estimated to be ca. 15%, based upon repeated measurements.

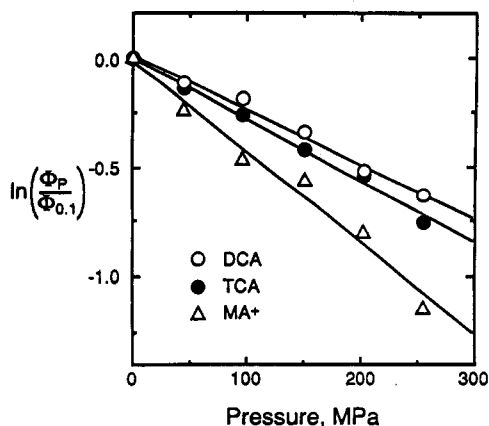
## Results

Quenching of the first excited singlet state of the uncharged acceptors 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA) with the alkylbenzene donors listed in Table I results in the formation of a geminate radical-ion pair ( $\text{A}^-(\text{S})\text{D}^{+\bullet}$ , Scheme I). The values of  $\Phi_{\text{ions}}$ , determined previously

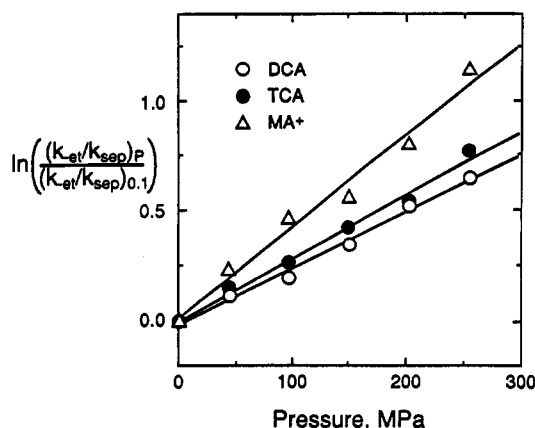


for these pairs at atmospheric pressure,<sup>3</sup> depend upon the rates of return electron transfer ( $k_{\text{et}}$ ), which in turn depend upon the exothermicity of the return electron-transfer reaction ( $\Delta G_{\text{et}}$ ), given by  $E_{\text{ox}}^{\text{D}} - E_{\text{red}}^{\text{A}}$  (vide infra).<sup>3</sup> The values of  $\Delta G_{\text{et}}$  summarized in Table I are calculated by using the redox parameters given in ref 3. *N*-Methylacridinium ( $\text{MA}^+$ ) has molecular dimensions, a ground-state reduction potential, a first excited-state energy, and an excited-state lifetime which are similar to those of TCA.<sup>16</sup> After electron-transfer quenching of the first excited state of  $\text{MA}^+$ , the resulting geminate pair consists of a neutral methylacridine radical and a radical cation. We have previously shown that the rates of the return electron-transfer processes in the radical anion/radical cation geminate pairs formed from the DCA and TCA and the neutral radical/radical cation geminate pairs from  $\text{MA}^+$  depend upon  $\Delta G_{\text{et}}$  in a similar manner.<sup>16</sup> However, we expect that electrostriction effects, in which the overall volume of a solvated ionic system changes with applied pressure,<sup>11</sup> should be different for the radical anion/radical cation and the neutral radical/radical cation pairs. The separation process,  $k_{\text{sep}}$ , may also be different for the two types of radical ion pairs, since in the former case there is a Coulombic barrier for separation whereas in the latter case the separation is controlled mainly by a diffusive barrier.

Values for  $\Phi_{\text{sep}}$  were measured for each of the donor/acceptor pairs listed in Tables I and II as a function of pressure, up to 256 MPa (1 MPa = 9.87 atm, 1 atm ca. 0.1 MPa). For each system the quantum yields decrease with increasing pressure (Figure 3). The measured activation volumes for  $\Phi_{\text{ions}}$  for the DCA and TCA systems ranged from +6.5 to +7.8  $\text{cm}^3 \text{mol}^{-1}$ , with the exception of the DCA/pentamethylbenzene pair, for which a value of ca. +9.5  $\text{cm}^3 \text{mol}^{-1}$  was obtained (Table I). The effect of pressure on the quantum yields was even more pronounced in the  $\text{MA}^+$  systems, for which activation volumes of +9.0 to +11.0  $\text{cm}^3 \text{mol}^{-1}$  were measured (Table II).



**Figure 3.** Representative plots showing the dependence of the yield of separated radical ions,  $\Phi_{\text{ions}}$ , as a function of pressure, plotted as the yield at the applied pressure ( $\Phi_p$ ) relative to the yield at atmospheric pressure ( $\Phi_{0.1}$ ), for (open circles) 9,10-dicyanoanthracene (DCA) with 1,2,3,4-tetramethylbenzene as donor, (closed circles) 2,6,9,10-tetracyanoanthracene (TCA) with 1,2,4-trimethylbenzene as donor, and (triangles) *N*-methylacridinium hexafluorophosphate ( $\text{MA}^+$ ) with mesitylene as the donor. The straight lines are obtained from a linear least-squares analysis.



**Figure 4.** Representative plots showing the dependence of the ratio of the rate constants  $k_{\text{et}}/k_{\text{sep}}$  as a function of pressure, plotted as the ratio at the applied pressure ( $(k_{\text{et}}/k_{\text{sep}})_p$ ) relative to the yield at atmospheric pressure ( $(k_{\text{et}}/k_{\text{sep}})_{0.1}$ ), for (open circles) 9,10-dicyanoanthracene (DCA) with 1,2,3,4-tetramethylbenzene as donor, (closed circles) 2,6,9,10-tetracyanoanthracene (TCA) with 1,2,4-trimethylbenzene as donor, and (triangles) *N*-methylacridinium hexafluorophosphate ( $\text{MA}^+$ ) with mesitylene as the donor. The straight lines are obtained from a linear least-squares analysis.

The values of  $\Phi_{\text{ions}}$  are related to the rate constants  $k_{\text{et}}$  and  $k_{\text{sep}}$  according to eq 2. Plots of  $k_{\text{et}}/k_{\text{sep}}$  versus pressure (Figure

$$\frac{k_{\text{et}}}{k_{\text{sep}}} = \frac{1}{\Phi_{\text{sep}}} - 1 \quad (2)$$

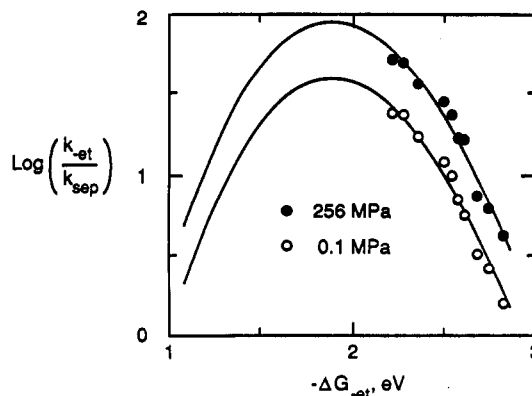
4) yield the composite activation volumes  $\Delta V^\ddagger(k_{\text{et}}/k_{\text{sep}})$  listed in Tables I and II.

## Discussion

The effect of external pressure for all of the donor/acceptor pairs is to decrease  $\Phi_{\text{ions}}$  as a consequence of an increase in the rate ratio  $k_{\text{et}}/k_{\text{sep}}$ . As discussed above, we have previously observed that  $k_{\text{et}}$  decreases as a function of the reaction exothermicity,  $\Delta G_{\text{et}}$ , due to the Marcus inverted region effect. The dependence of  $k_{\text{et}}$  on  $\Delta G_{\text{et}}$  was analyzed previously by using a golden rule type expression, eq 3, in which the rate is given as

$$k_{\text{et}} = \left( \frac{\pi}{\hbar^2 \lambda_s k_B T} \right)^{1/2} V^2 \sum_{j=0}^{\infty} \frac{e^{-S} S^j}{j!} \exp \left[ -\frac{(j h \nu_v + \Delta G_{\text{et}} + \lambda_s)^2}{4 \lambda_s k_B T} \right] \quad (3)$$

$$S = \lambda_v / h \nu_v$$



**Figure 5.** Plots of  $\log(k_{\text{et}}/k_{\text{sep}})$  versus  $\Delta G_{\text{et}}$ , for reactions of the radical anion/radical cation pairs formed from quenching the excited cyanoanthracene sensitizers, at atmospheric pressure and at 256 MPa. The curves are calculated by using eq 3, using the parameters described in the text.

the product of an electronic coupling matrix element squared ( $V^2$ ) and a Franck-Condon term, which includes the dependence of the rate on the reaction exothermicity,  $\Delta G_{\text{et}}$ , and on low-frequency (mainly solvent) and high-frequency (skeletal vibrational) reorganization energies,  $\lambda_s$  and  $\lambda_v$ .<sup>3,17</sup> The rearranged high-frequency vibrations are represented by a single averaged frequency  $\nu_v$ . The quantum yield experiments do not give the rate of the return electron-transfer reaction, but the rate ratio ( $k_{\text{et}}/k_{\text{sep}}$ ). We make the reasonable assumption that only the rates of the electron-transfer reactions,  $k_{\text{et}}$ , and not that of the separation process,  $k_{\text{sep}}$ , vary with the reaction exothermicity,  $\Delta G_{\text{et}}$ .<sup>3</sup> We further assume that  $k_{\text{sep}}$  is a constant for the different donors, which were chosen to have structures which are as similar as possible but have different oxidation potentials.<sup>3</sup> Figure 5 is a plot of  $\log(k_{\text{et}}/k_{\text{sep}})$  as a function of  $\Delta G_{\text{et}}$  for the reactions of the radical anion/radical cation pairs from the cyanoanthracene sensitizers, at atmospheric pressure and at 256 MPa. The data at the high pressure are calculated by using the values of  $\Delta V^\ddagger(k_{\text{et}}/k_{\text{sep}})$  given in Table I. The data at atmospheric pressure are taken from previously published work, in which several radical ion pairs not included in the present work were studied.<sup>3</sup> According to eq 3, the shape of a plot of  $\log(k_{\text{et}})$  versus  $\Delta G_{\text{et}}$  is determined by the parameters related to the vibrational and solvent reorganization,  $\lambda_s$ ,  $\lambda_v$ , and  $\nu_v$ . The matrix element  $V$  is only a scaling parameter for the electron-transfer rates. Therefore, although we do not know the absolute rates of the return electron-transfer reactions, the influence of pressure on the reorganization parameters can in principle be obtained from changes in the shape of a plot of  $\log(k_{\text{et}}/k_{\text{sep}})$  versus  $\Delta G_{\text{et}}$  with pressure. The curve drawn through the points for the reactions at atmospheric pressure was calculated by using values for the reorganization parameters which give the best fit to the electron transfer and related spectroscopic data, as detailed previously.<sup>3</sup> The values used are 1.72 eV, 0.2 eV, and 1400  $\text{cm}^{-1}$  for  $\lambda_s$ ,  $\lambda_v$ , and  $\nu_v$ , respectively. The vertical displacement of the curve is determined for these data by taking values of 10.8  $\text{cm}^{-1}$  and  $5 \times 10^8 \text{ s}^{-1}$  for  $V$  and  $k_{\text{sep}}$ , respectively.<sup>3</sup> The solid curve drawn through the data at high pressure was calculated by using the same values for the reorganization parameters used at atmospheric pressure and was rescaled in the vertical direction. The fact that the data at high pressure can be fitted by using the same reorganization parameters as at atmospheric pressure suggests that the pressure dependence of the reorganization parameters is small in these systems.

The activation volumes for the rate ratio ( $k_{\text{et}}/k_{\text{sep}}$ ),  $\Delta V^\ddagger(k_{\text{et}}/k_{\text{sep}})$ , are related to the activation volumes of the individual rate constants by eq 4. In a simple analysis it can be assumed

(17) (a) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* 1974, 71, 3640. (b) Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* 1974, 5, 183. (c) Ulstrup, J.; Jortner, J. J. *Chem. Phys.* 1975, 63, 4358. (d) Siders, P.; Marcus, R. A. J. *Am. Chem. Soc.* 1981, 103, 741, 748. (e) Brunschweig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. J. *Am. Chem. Soc.* 1980, 102, 5798.

$$\Delta V^\ddagger(k_{-et}/k_{sep}) = \Delta V^\ddagger(k_{-et}) - \Delta V^\ddagger(k_{sep}) \quad (4)$$

that the separation process,  $k_{sep}$ , is diffusion controlled, and therefore depends inversely upon viscosity.<sup>18</sup> This is almost certainly a reasonable assumption for the neutral radical/radical cation pairs formed from the acridinium sensitizer for which there is no Coulombic barrier to separation. The change in the viscosity of acetonitrile as a function of applied pressure is known,<sup>19</sup> from which an activation volume for diffusion-controlled separation of  $+8 \text{ cm}^3 \text{ mol}^{-1}$  can be determined.<sup>19</sup> Other effects could be taken into account for the separation of the radical anion/radical cation pairs. Eigen has discussed the rate of separation of an anion and a cation in terms of the solvent viscosity and dielectric constant.<sup>20</sup> For a solvent-separated radical ion pair in acetonitrile, however, the influence on  $k_{sep}$  of the change in viscosity with pressure is much larger than the corresponding influence of the change in dielectric constant. Rather than place too much emphasis on apparently small differences in the values of  $\Delta V^\ddagger(k_{sep})$ , therefore, we assume that a value of  $+8 \text{ cm}^3 \text{ mol}^{-1}$  is appropriate for both the radical anion/radical cation and neutral radical/radical cation pairs. The rates of separation for both geminate pairs are predicted to have positive activation volumes, despite steady-state equilibrium observations that the reaction volumes for ion pair separation are largely negative, due to the electrostriction effect.<sup>11c-e</sup>

The average values of  $\Delta V^\ddagger(k_{-et}/k_{sep})$  are ca.  $-8 \text{ cm}^3 \text{ mol}^{-1}$  and ca.  $-11 \text{ cm}^3 \text{ mol}^{-1}$  for the geminate pairs derived from the cyanoanthracene and acridinium acceptors, respectively (Tables I and II). Thus, by taking a value for  $\Delta V^\ddagger(k_{sep})$  of  $+8 \text{ cm}^3 \text{ mol}^{-1}$  and using eq 4, values for  $\Delta V^\ddagger(k_{-et})$  of 0 and  $-3 \text{ cm}^3 \text{ mol}^{-1}$  are obtained for the radical anion/radical cation and neutral radical/radical cation pairs, respectively. The lack of an activation volume for the radical anion/radical cation reaction indicates that there is no discernible pressure dependence for  $k_{-et}$  in this case (perhaps due to a cancellation of effects, vide infra). The small negative activation volume for the neutral radical/radical cation pair suggests that in this case the return electron-transfer rate increases slightly with increasing pressure. Obviously the activation volumes of the individual reactions  $k_{sep}$  and  $k_{-et}$  are based upon assumptions, and it is difficult to estimate the errors associated with their absolute values. However, it is clear that the quantum yield data are most easily understood if the activation volumes for the return electron-transfer processes ( $k_{-et}$ ) are essentially zero or have small negative values. Using  $+8 \text{ cm}^3 \text{ mol}^{-1}$  for  $\Delta V^\ddagger(k_{sep})$ , a value for  $k_{sep}$  at 256 MPa of  $2.2 \times 10^8 \text{ s}^{-1}$  can be calculated. Indeed, the curve through the data at the high pressure shown in Figure 5 was obtained by using this value for  $k_{sep}$ , and the same values for the parameters  $\lambda_s$ ,  $\lambda_v$ ,  $\nu$ , and  $V$  were used to fit the data at atmospheric pressure. The good fit emphasizes the fact that by fitting the data in the form shown in Figure 5 it is not possible to clearly discern any effect of external pressure on these parameters for the radical anion/radical cation pairs.

As in previous studies of pressure effects on electron-transfer processes we can consider the contributions to  $\Delta V^\ddagger(k_{-et})$  from each of the parameters which influence the electron-transfer reaction.<sup>13,15</sup> As before,<sup>13,15</sup> changes in the internal reorganization energies and vibrational frequencies are assumed to be negligible over the pressure range studied here, and thus we consider the influence of pressure on  $\Delta G_{-et}$ ,  $\lambda_s$ , and  $V$  only.

The electron-transfer reaction free energy ( $-\Delta G_{-et}$ ) is obtained by using eq 5 in which  $E^{\text{ox}}_D$  and  $E^{\text{red}}_A$  are the electrochemical oxidation and reduction potentials of the donor and acceptor. A

$$-\Delta G_{-et} = E^{\text{ox}}_D - E^{\text{red}}_A \quad (5)$$

Coulomb term is often included in relations such as this, which takes into account the decrease in  $-\Delta G_{-et}$  due to the stabilizing effect of the opposing charges.<sup>21</sup> For solvent-separated radical-ion

pairs in acetonitrile at atmospheric pressure, in which the distance between the ions is ca.  $6\text{--}8 \text{ \AA}$ , this stabilization amounts to only ca. 60 mV, which is small compared to the overall  $\Delta G_{-et}$  (Table I), and was therefore neglected in previous studies on these systems.<sup>3</sup> The dielectric constant of acetonitrile increases somewhat with pressure,<sup>19</sup> which might be expected to slightly decrease  $-(\Delta G_{-et})$ . However, previous electrochemical studies on the present systems<sup>3</sup> suggest that for small changes in dielectric constant, as in the present case, the decrease in the redox energy of the pairs will be negligible. In addition, the Coulombic stabilization will also tend to decrease in a medium of higher dielectric constant.<sup>21</sup> For these reasons the effect of pressure on  $\Delta G_{-et}$  is considered to be negligible and the data in Figure 5 are plotted with the assumption that  $\Delta G_{-et}$  is the same at atmospheric pressure and at 256 MPa. Any decrease in  $-(\Delta G_{-et})$  in the higher polarity medium would, however, tend to reduce the exothermicity of the return electron-transfer processes. Due to the inverted region effect this would result in an increase in reaction rate and thus a small negative contribution to  $\Delta V^\ddagger(k_{-et})$ .

The solvent reorganization energy,  $\lambda_s$ , is usually described according to a dielectric continuum model, eq 6, in which the reorganization energy is given in terms of the solvent refractive index,  $n$ , and the solvent dielectric constant,  $\epsilon$ .<sup>9</sup> The pressure

$$\lambda_s = \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r_{DA}} \right) \left( \frac{1}{n^2} - \frac{1}{\epsilon} \right) \quad (6)$$

dependence of  $\lambda_s$  is most simply estimated with this equation by assuming that the interion distance ( $r_{DA}$ ) and the ionic radii ( $r_A$  and  $r_D$ ) do not change with pressure.<sup>15</sup> The pressure dependence of  $\lambda_s$  is thus given by the pressure dependencies of the solvent refractive index, and the dielectric constant.

If the pressure affects only the bulk solvent parameters  $n$  and  $\epsilon$ , then using eq 6 and the data in refs 19 we find that  $\lambda_s$  in acetonitrile at 256 MPa should be smaller than at atmospheric pressure by a factor of 0.92, i.e., a decrease from 1.72 to 1.58 eV. It is important to note that unlike other electron-transfer reactions whose pressure dependence has been studied, because the return electron-transfer reactions are in the inverted region, a decrease in reorganization energy leads to a decrease in reaction rate. Thus, if only the properties of the solvent are considered, the dielectric continuum model predicts that the pressure dependence of  $\lambda_s$  should result in a positive contribution to  $\Delta V^\ddagger(k_{-et})$ . However, as indicated above, the data are consistent with no change in  $\lambda_s$  when plotted in the form shown in Figure 5. If the change in rate ( $\log(k_{-et})$ ) with driving force ( $\Delta G_{-et}$ ) in the inverted region is approximated by a straight line, then the slope of such a line over any particular range of  $\Delta G_{-et}$  is determined by the magnitude of the reorganization energy, becoming steeper with decreasing reorganization energy for data in the inverted region. A plot of the electron-transfer data at high pressure versus corresponding data at atmospheric pressure, therefore, represents a sensitive method of determining whether the reorganization energy changes with applied pressure. The slope of such a plot, again approximating to a straight line, is unity if there is no change in reorganization energy, is greater than unity if the reorganization energy is smaller at the higher pressure, and is less than unity if the reorganization energy is higher at the higher pressure. The rate ratios ( $k_{-et}/k_{sep}$ ) (i.e.,  $(\Phi_{\text{ions}}^{-1} - 1)$ , eq 2) for the various values of  $\Delta G_{-et}$  at high pressure are plotted in logarithmic form versus the corresponding ratios at atmospheric pressure for both sets of geminate pairs in Figure 6. The straight-line approximation appears to be reasonable over the  $\Delta G_{-et}$  range of the present data. If  $\lambda_s$  decreases with pressure from 1.72 to 1.56 eV, as predicted by the dielectric continuum theory, then the slopes of both plots should be 1.27. In fact the slopes are 0.94 and 0.90 for the cyanoanthracene and  $\text{MA}^+$  data, respectively.<sup>22</sup> The fact that the slopes are only slightly less than unity suggests that in each case  $\lambda_s$  either does not change, or actually increases somewhat, with pressure.<sup>22</sup> The dielectric

(18) Leffler, J.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; Wiley: New York, 1963.

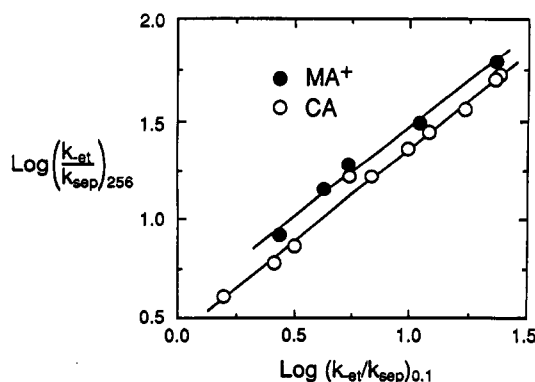
(19) (a) Fetterolf, M. L.; Offen, H. W. *J. Phys. Chem.* **1988**, *92*, 3437.

(b) Srinivasan, K. R.; Kay, R. L. *J. Solution Chem.* **1977**, *6*, 357.

(20) Eigen, M. *Z. Phys. Chem. (Wiesbaden)* **1954**, *1*, 176.

(21) Weller, A. *Z. Phys. Chem. (Wiesbaden)* **1982**, *133*, 93.

(22) The error in  $\Delta V^\ddagger(k_{-et}/k_{sep})$  is ca.  $1 \text{ cm}^3 \text{ mol}^{-1}$ , which results in an error in the slope of a plot of the type shown in Figure 6 of ca. 0.1.



**Figure 6.** Plots of  $\log(k_{\text{et}}/k_{\text{sep}})$  at 256 MPa versus the corresponding data at atmospheric pressure for (closed circles) neutral radical/radical cation pairs from *N*-methylacridinium hexafluorophosphate ( $\text{MA}^+$ ) as excited-state electron acceptor and (open circles) radical anion/radical cation pairs from the neutral cyanoanthracenes as excited-state electron acceptors. The straight lines are obtained from a linear least-squares analysis with slopes of 0.90 and 0.94 for the acridinium and cyanoanthracene sensitizer data, respectively.

continuum model clearly overestimates the decrease in  $\lambda_s$  with pressure for the systems studied here. The bulk density of acetonitrile does increase by a factor of 1.16 at 256 MPa compared to atmospheric pressure, however.<sup>19b</sup> Such a change in the density would result in a corresponding decrease in  $r_{\text{DA}}$  of ca. 5%. According to eq 6, however, any decrease in  $r_{\text{DA}}$  should further reduce  $\lambda_s$ , in contrast to the observations. An increase in the solvent density should also increase the density of solvent molecules surrounding the ions in the solvent-separated pairs. Such a phenomenon, however, is not taken into account by the dielectric continuum model. In this model the charges are assumed to be represented by spheres about the reactants, within which the dielectric is saturated and outside which the dielectric is unsaturated.<sup>9</sup> For polyatomic species such as those used in the present study it is normally assumed that the diffuse nature of the charge results in negligible saturation of the dielectric around the ions, and therefore the radii in eq 6 are taken simply to be equal to the radii of the ions.<sup>9a</sup> However, if the dielectric were to be partially saturated, then the radius should presumably include part of the first solvent shell.<sup>23</sup> Under such circumstances, any increase in the density of the solvent around the reactants would presumably result in a decrease in the effective radius of the dielectric saturation, which, according to eq 6 would result in a decrease in  $\lambda_s$ . This appears to be the most reasonable way of explaining the data within the framework of the continuum model. If  $\lambda_s$  does not change with pressure then the influence of the decreased radius offsets the influence of the refractive index and dielectric constant. If  $\lambda_s$  actually increases then the influence of the former is greater than the latter.

Additional contributions to  $\Delta V^*(k_{\text{et}})$  come from the electronic coupling matrix element,  $V$ , which is usually considered to depend exponentially on the distance between the species undergoing electron transfer (eq 7).<sup>17</sup> Since the electron-transfer rate depends

$$V_1 = V_2 e^{-(\beta(r_1-r_2)/2)} \quad (7)$$

(23) In a recent model for electron-transfer reactions it has been suggested that the dielectric might be fully saturated around ionic reactants: Kakitani, K.; Mataga, N. *J. Phys. Chem.* **1985**, *89*, 8.

upon the value of  $V^2$  (eq 3), if the separation distance within the pair increases, then the rate should decrease which would result in a positive contribution to  $\Delta V^*(k_{\text{et}})$ . Correspondingly, if the separation distance decreases, the rate  $k_{\text{et}}$  increases resulting in a negative contribution to  $\Delta V^*(k_{\text{et}})$ . As discussed above, the density of acetonitrile increases with applied pressure. Thus from simple free-volume arguments we expect that the separation of the ions will decrease with pressure, resulting in a negative contribution to  $\Delta V^*(k_{\text{et}})$ . However, equilibrium measurements indicate that external pressure promoted a transformation from tight to loose ion pairs due to the electrostriction effect,<sup>11c-e</sup> which suggests that the separation distance in a radical ion pair might increase with pressure. The fit to the data of the radical anion/radical cation pairs shown in Figure 5 suggests that  $V$  does not change for these pairs, implying that the center-to-center distance  $r_{\text{DA}}$  does not change with pressure. This would be consistent with the electrostriction effect acting to oppose the decrease in distance expected by the decrease in bulk density. Electrostriction effects are minimal for the neutral radical/radical cation pairs derived from the  $\text{MA}^+$  sensitizer, however, since there is no change in charge upon electron transfer from donor to acceptor. For these geminate pairs, all of the return electron-transfer reactions appear to have negative activation volumes. Based upon the discussion above it is clear that the most likely negative contribution to the overall  $\Delta V^*(k_{\text{et}})$  arises from an increase in  $V$  due to a decrease in the separation distance within the geminate pair, which would not be "inhibited" in this case by electrostriction effects. The negative contribution from  $V$  must more than offset any positive contribution from  $\lambda_s$  for the geminate pairs in these cases, since any decrease in  $r_{\text{DA}}$  must also decrease  $\lambda_s$ .

## Conclusions

The quantum yields for formation of free-radical ions from photoinduced geminate radical ion pairs in acetonitrile at room temperature decrease as a function of external pressure. At an applied pressure of 256 MPa, the quantum yields decrease by an average value of ca. 2.3 for the radical anion/radical cation pairs from the neutral cyanoanthracene sensitizers, and by an average value of ca. 3.1 for the neutral radical/radical cation pairs from the acridinium sensitizer. These dependencies are best understood as arising mainly from a decrease in the rate of separation within the pairs as the viscosity increases. The solvent reorganization energy does not decrease in the manner which would be predicted from simple considerations of the dielectric nature of the solvent but remains unchanged or slightly increases. It is suggested that pressure-induced changes in the radius of the sphere of dielectric saturation might account for these observations. The pressure effects for the neutral radical/radical cation pairs are larger than those for the radical anion/radical cation pairs. These effects are best explained as being due to an increase in the electronic coupling matrix element in the former cases. A similar increase is not observed for the radical anion/radical cation pairs due to the electrostriction effect.

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**Registry No.** DCA, 1217-45-4; TCA, 80721-78-4; *N*-methylacridinium, 13367-81-2; 1,2,4-trimethylbenzene, 95-63-6; 1,2,3,4-tetramethylbenzene, 488-23-3; durene, 95-93-2; pentamethylbenzene, 700-12-9; *m*-xylene, 108-38-3; mesitylene, 108-67-8; *p*-xylene, 106-42-3.