

An Electron Spin Resonance Study of Counterion Effects on the Rate Constant of Disproportionation of the Cyclooctatetraene Anion

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Abstract: An esr study has been made of the counterion effect on the electron transfer reaction $2\text{COT}^- \xrightarrow{k} \text{COT} + \text{COT}^{2-}$. A nonequilibrium COT^- concentration could be created using the photoelectron transfer reaction $\text{COT}^{2-} + \text{COT} + h\nu \rightarrow 2\text{COT}^-$. The results show that k increases strongly with increasing counterion radius. Similar trends have previously been found in electron transfer reactions involving transition metal complexes. They are attributed to the role of the counterion as the bridging group between two anions in the activated complex.

By subjecting a solution of A^{2-} , A^- , and A , where A is an aromatic molecule, involved in the disproportionation equilibrium



to near-uv irradiation, one can induce an increase in A^- concentration by photooxidation of A^{2-} .¹

This provides a convenient way to study the kinetics of the disproportionation or electron transfer reaction involving two mononegative ions. Studies of the kinetics of disproportionation reactions are of some interest since they may contribute to our understanding of electron transfer mechanisms, which continue to be the subject of extensive investigations especially in inorganic chemistry.²

Here we report the results of an esr investigation of the counterion effects on the kinetics of disproportionation of the cyclooctatetraene (COT) radical anion in methyltetrahydrofuran (MTHF).

It is found that the counterion effects parallel, at least qualitatively, trends observed in electron transfer reactions between inorganic ions, for instance³



Experimental Section

The solvents, methyltetrahydrofuran (MTHF) and 1,2-dimethoxyethane (DME), were dried over calcium hydride, vacuum distilled, and stored over Na-K alloy before use. COT (Chemical Procurement Laboratories) was used without further purification. Lithium tetraphenylboron was prepared according to the method reported by Bhattacharyya, *et al.*⁴ Samples were prepared according to standard procedures⁵ in an all-glass evacuated apparatus. Unless stated otherwise the initial COT concentration was between 5×10^{-2} and 5×10^{-1} mol; the solutions were reduced with Li, Na, K, Rb, or Cs until $[\text{COT}] \approx [\text{COT}^{2-}]$. In the temperature range of interest the $[\text{COT}^-]$ concentrations were negligibly small in the absence of light (the disproportionation equilibrium constant is of the order of 10^9 or larger).

Esr spectra were recorded with a Varian V4502 spectrometer with a 9 in. magnet, equipped with a variable-temperature accessory. Temperatures were measured with a copper-constantan thermocouple and could be maintained constant within $\pm 1^\circ$.

- (1) A. G. Evans and J. C. Evans, *J. Chem. Soc. B*, 271 (1966).
- (2) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970.
- (3) J. C. Sheppard and A. C. Wahl, *J. Amer. Chem. Soc.*, **79**, 1020 (1957).
- (4) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965).
- (5) D. E. Paul, Ph.D. Thesis, Washington University, 1954.

Special flat quartz cells fitting in the low temperature insert of the cavity were used in the experiments. To minimize concentration gradients of the photoproducts across the cells the path length was kept small (either 1 mm or 0.1 mm). The kinetic data did not vary significantly with cell path length.

A Philips SP 500 high-pressure Hg arc was used as light source for the *in situ* radiation experiments. The light was focussed on the optical window of the cavity with glass lenses and a CuSO_4 solution was used as heat filter. Long-term irradiation of COT^- - COT^{2-} solutions did not result in noticeable decomposition.

Results

Characterization of the Spectra. During *in situ* irradiation of the solutions the Li, Na, and K samples gave rise to photosignals which could be from $5\times$ to as much as $1000\times$ the background signal in the absence of light in the temperature range from -60 to -130° . For the Rb system the maximum photosignal (around -130°) was about $3\times$ the background signal. Irradiation of the Cs system did not result in a detectable signal.

The Li reduced samples gave rise to a nine-line spectrum with a proton hyperfine splitting constant (hfsc) of 3.17 G and a peak-to-peak line width of 0.06 G. Over the temperature range studied no sign of Li hfs was found. Hence we were dealing with free COT^- anions or loose ion pairs in which the spin density at the Li nuclei is zero.

The esr photosignals of the Na reduced samples could be assigned to the $\text{COT}^- \cdot \text{Na}^-$ ion pair. The Na hfsc was 0.96 G and showed no temperature dependence; the peak-to-peak line width in the spectra was 0.40 G.

The K reduced samples gave rise to nine broad lines (1.5 G line width) with indications of unresolved K hfs. The spectrum is assigned to the $\text{COT}^- \cdot \text{K}^+$ ion pair.

The radical ions created by irradiation of the Rb system did not give rise to a resolved esr spectrum. The presence of two Rb isotopes with nuclear spin probably accounts for this fact.

The hyperfine data derived from the spectra agree quite well with those reported by Strauss, *et al.*⁶ Strauss cites substantially larger line widths, however. It seems likely that the slower electron transfer rates between anions and dianions in the temperature range of interest here accounts for this fact. It has been

- (6) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **85**, 2360 (1963).

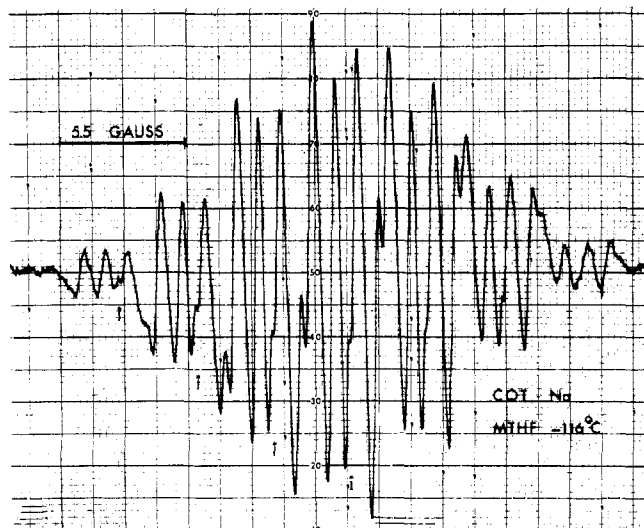


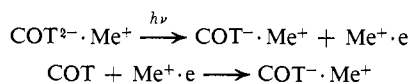
Figure 1. Photosignal produced by the COT-Na system if only a trace of COT^{2-} is present in solution. The magnetic field increases from left to right. The COT^- lines are marked. The lines in the wings of the spectrum are not shown.

shown that electron transfer between anion and COT is too slow to make a contribution to the line width.⁷

The Photooxidation Process. Under the conditions outlined before, no superposition spectra of free anions and ion pairs were recorded. This is of some interest in the case of the Na, K, and Rb systems since a photo-induced electron transfer could create free anions even



if the ion pair is the thermodynamically more stable species. One predicts that the ion pairing rate constant is much larger than the disproportionation rate constant. Moreover, if a fraction of the dianions is not associated with two counterions the excess free Me^+ would increase the rate of conversion of COT^- in $\text{COT}^- \cdot \text{Me}^+$. Hence, the thermodynamically more stable $\text{COT}^- \cdot \text{Me}^+$ can be expected to dominate the esr spectra under continuous irradiation conditions. It is noteworthy, however, that attempts to enhance the relative free anion signal by using modulated light (with frequencies up to 100 Hz) and a second phase sensitive detector, while largely suppressing the $\text{COT}^- \cdot \text{Me}^+$ signal at low temperatures, failed to confirm the creation of COT^- . We estimate that if the photooxidation mechanism indeed involves a free electron, the ion pairing rate should be at least two orders of magnitude larger than the disproportionation rate. An alternative mechanism which could explain the results involves the transfer of alkali cation-electron "ion pairs."^{8,9}



COT^- - $\text{COT}^- \cdot \text{Na}^+$ superposition spectra could be obtained when only a trace of COT was reduced. The representative spectrum depicted in Figure 1 shows that the ion pair has a higher g value than the free ion

(7) T. J. Katz, *J. Amer. Chem. Soc.*, **82**, 3784, 3785 (1960).

(8) L. J. Gilling, J. G. Kloosterboer, R. P. H. Rettschnick, and J. D. W. van Voorst, *Chem. Phys. Lett.*, **8**, 457 (1971).

(9) M. Fisher, G. Ramme, S. Claesson, and M. Szwarc, *ibid.*, **9**, 309 (1971).

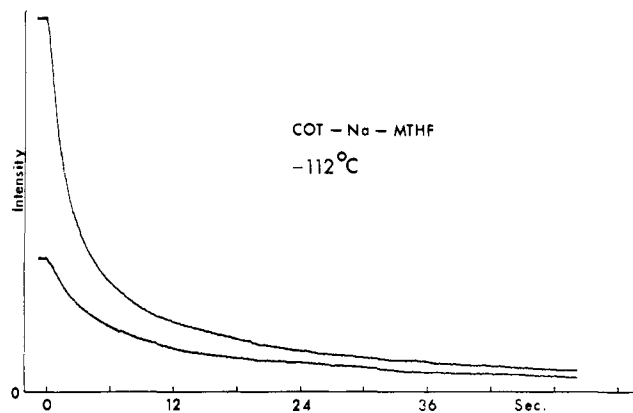


Figure 2. Effect of $\text{COT}^- \cdot \text{Na}^+$ concentration during irradiation upon $\tau_{1/2}$.

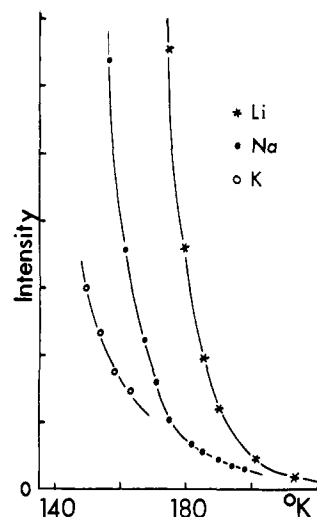


Figure 3. Variations of the esr intensities for the Li, Na, and K systems as a function of temperature during irradiation. Differences in heights between different systems do not give quantitative concentration differences.

($\Delta g \approx 10^{-4}$); similar counterion induced shifts have been reported previously.¹⁰ The COT^- signal disappears upon further reduction, indicating that not all the dianions are associated with two counterions.

The photooxidation threshold of COT^{2-} lies around 4000 Å; similar values have been reported for other aromatic dianions.¹¹ The photosignal intensity was found to be proportional to the square root of the number of photons, indicating a one-photon oxidation process.

The Disproportionation Mechanism and Kinetics. The decay of the esr signals following irradiation closely followed second-order kinetics with respect to the paramagnetic species (COT^- or $\text{COT}^- \cdot \text{Me}^+$). Figure 2 illustrates the relation between initial radical concentration (during irradiation) and $\tau_{1/2}$, the time required for decay to half the initial concentration.

Figure 3 depicts the photosignal intensity variation with temperature for the Li, Na, and K systems. Rb reduced COT solutions qualitatively showed the same temperature dependence. The poor signal-to-noise and limited temperature range over which the system

(10) W. G. Williams, R. J. Pritchett, and G. K. Fraenkel, *J. Chem. Phys.*, **52**, 5584 (1970).

(11) J. D. W. van Voorst and G. J. Hoijtink, *ibid.*, **42**, 3995 (1965).

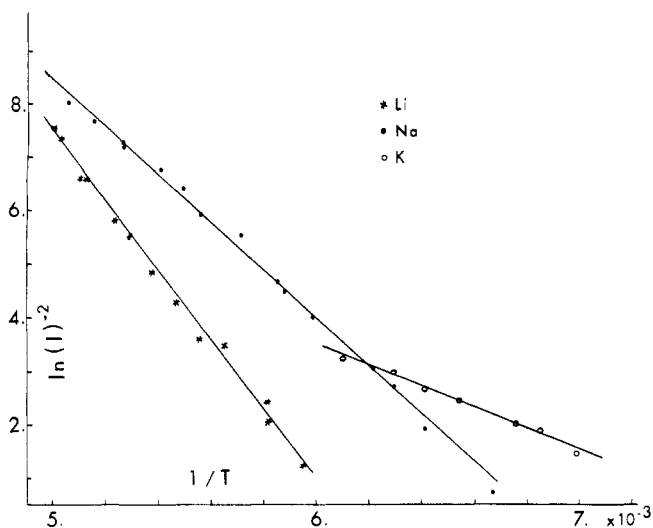


Figure 4. $\ln [\text{COT}^-]^{-2}$ vs. $1/T$ for the Li, Na, and K systems.

could be studied precluded accurate measurements for this system. The amplitudes of the signals were taken as a measure of the radical concentrations (the line widths remained constant). Corrections were made for the Curie temperature dependence. In general the radical ion concentration at any given temperature during irradiation decreased in the series Li, Na, K, Rb, and possibly Cs.

Activation energies for the disproportionation reactions were derived from plots of $\ln \{[\text{COT}^-] \tau_{1/2}\}^{-1}$ vs. $1/T$ and/or $\ln [\text{COT}^-]^{-2}$ vs. $1/T$. Here $[\text{COT}^-]$ stands for the radical ion (free ion or ion pair) concentration during irradiation. The latter method assumes that k (the disproportionation rate constant) is proportional to $[\text{COT}^-]^{-2}$. This will be the case if the photooxidation rate constant is independent of temperature and both COT and COT^{2-} are present in large excess (a condition which was always fulfilled). Since both methods gave activation energy (E_a) values which agreed within experimental uncertainty, the second method is justified. It has the advantage that the E_a for the K reduced systems could be determined. In this system $\tau_{1/2}$ above -124° becomes too short to be measured with our equipment.

Table I summarizes the E_a values, while Figure 4

Table I. Activation Energies and Rate Constants for the Disproportionation Reaction

	E_a , kcal mol ⁻¹	k , mol ⁻¹ sec ⁻¹
Li ⁺	13 ± 1	$3 \times 10^2 (-100^\circ)$
Na ⁺	9 ± 1.5	$\begin{cases} 6 \times 10^4 (-100^\circ) \\ 2 \times 10^3 (-126^\circ) \end{cases}$
K ⁺	3.6 ± 0.5	$5 \times 10^6 (-124^\circ)$
Rb ⁺	a	$\approx 5 \times 10^6 (-125^\circ)^b$

^a The temperature dependence of the photosignal could be followed only over a limited temperature range; no E_a value could be derived. ^b k derived indirectly from photosignal intensity (see text).

shows the Arrhenius plots derived from the signal intensity variations with temperature during irradiation. It was found that the slopes of the curves were independent of COT, COT^- , and COT^{2-} concentrations.

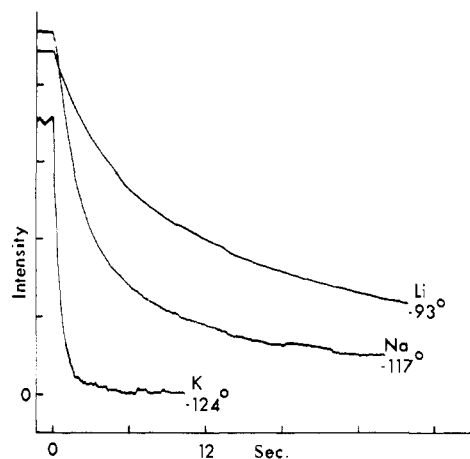


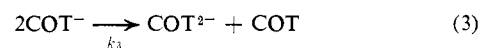
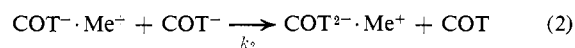
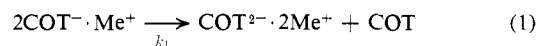
Figure 5. Decay of Li^- - COT^- , Na^+ - COT^- , and K^+ - COT^- photosignals. The concentrations at time zero were: Li, 0.2×10^{-3} mol; Na, 0.7×10^{-4} mol; K, 0.9×10^{-5} mol.

Rate constants were determined using the formula $k = \{[\text{COT}^-] \tau_{1/2}\}^{-1}$. $[\text{COT}^-]$, the radical concentration during irradiation, was determined by double integration of the second derivative esr signal and comparison with a DPPH standard. It was found that $k = C/[\text{COT}^-]^2$, where C is a constant independent of cation.¹² This enabled us to get good estimates of the values of the rate constants for the K and Rb systems when $\tau_{1/2}$ could not be determined experimentally. The rate constants are summarized in Table I. The dramatic change in decay rates going from Li to K is illustrated in Figure 5.

It must be emphasized that the derivation of the rate constants is based on the assumption that only the species giving rise to the esr spectrum are directly involved in the disproportionation reaction. This is not necessarily true, a point that will be addressed in the Discussion.

Discussion

The following reactions have to be considered in interpreting the experimental results.



The esr spectra obtained from the Na and K reduced COT solutions showed that no noticeable amount of free anion is present. Although the Rb system did not give rise to a spectrum in which Rb hfs could be discerned, free anions must be absent in this system as well. Usually ion pairing equilibrium constants for aromatic anions increase with increasing cationic radius.⁴ Moreover, even small amounts of COT^- would be readily observable in the esr spectra due to the reduced number of hyperfine lines.

We conclude that for the above three systems the kinetic data summarized in the table refer to the electron transfer between two ion pairs (reaction 1). This conclusion is supported by the effect of the addition of

(12) Indicating that the photooxidation rate constant of COT^{2-} is independent of the counterion.

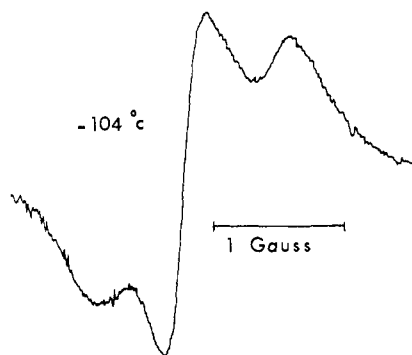


Figure 6. Center lines of the $\text{COT}^{\cdot-}\text{K}^+\text{-COT}^-$ spectrum during irradiation. $\text{COT}^{\cdot-}$ obtained by exchange of K^+ in MTHF solution with Li^+ in solid lithium tetraphenylboron.

traces of DME ($[\text{DME}] \approx [\text{COT}^{2-}]$ or smaller) on the disproportionation rate. It was found that significant reductions in the disproportionation rate could be achieved by additions of traces of DME to sodium reduced COT solutions in MTHF. Simultaneously the $\text{COT}^{\cdot-}\text{Na}^+$ ion pair spectrum was gradually replaced by the nine-line COT^- spectrum. In pure DME, where only the COT^- spectrum is observed, the rate constant for the COT^- decay at -75° (assuming that the reaction is second order in COT^-) was found to be of the order of $1 \text{ mol}^{-1} \text{ sec}^{-1}$. The data showed that $k_3 \ll k_1$ and $k_2 \leq k_1$.

The table shows that k_1 increases strongly in the series Na^+ , K^+ , Rb^+ . In accordance with this the steady-state photosignal intensity at a given temperature shows a strong decrease in this series, so that for the Rb^+ system it is only detectable at the lowest temperatures. Thus, the fact that no photosignal was observed for Cs-COT may reflect the fact that k_1 increases still more for this system.

The interpretation of the kinetic data for the Li reduced COT solutions is less straightforward. It was observed that the addition of excess lithium tetraphenylboron to a Li reduced COT solution, while not affecting the esr signal noticeably, increased the radical ion decay rate by roughly a factor of 2. We propose that the ion pairing equilibrium 4 lies strongly to the left for this system and that k_3 is very small (possibly zero) so that the decay is governed by the small concentration of ion pairs present in solution (via (2) and/or (1)).

The following experimental data are in agreement with this interpretation and, in addition, provided more information regarding the relative magnitudes of k_1 , k_2 , and k_3 .

After reducing about half of a $10^{-1} M$ solution of COT in MTHF with K, a fraction of the potassium cations was replaced by lithium cations by exchange of K^+ in solution with Li^+ in undissolved Li tetraphenylboron. The resulting solution gave rise to a photosignal consisting of a superposition of a broad and a narrow nine-line spectrum, due to $\text{COT}^{\cdot-}\text{K}^+$ and COT^- , respectively. The center portion of a typical spectrum is shown in Figure 6. The decay curves, of which an example is shown in Figure 7, showed an initial rapid decrease in radical concentration (characteristic for $\text{COT}^{\cdot-}\text{K}^+$) followed by a much slower decay.

It should be noted that for the COT-Na system, where $\text{COT}^{\cdot-}\text{Na}^+\text{-COT}^-$ mixtures were created by

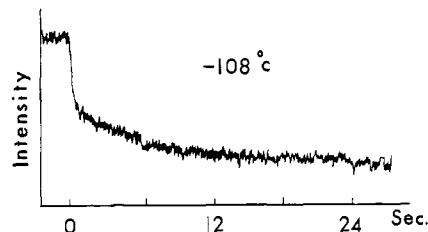


Figure 7. Typical decay curve given by the $\text{COT}^{\cdot-}\text{K}^+\text{-COT}^-$ system in MTHF.

addition of traces of DME, no such decay behavior was observed. In that case simple second-order decay curves were recorded.

This remarkable difference in behavior can be readily explained if $k_1 > k_2 > k_3$ and the ion pairing rate constant is large compared to k_1 .

Consider the $\text{COT}^{\cdot-}\text{Na}^+\text{-COT}^-$ system. Disproportionation takes place primarily via (1). The ion pairing equilibrium is maintained during decay since free Na^+ is available. A second-order decay results and $\tau_{1/2}$ is determined by $[\text{COT}^{\cdot-}\text{Na}^+]$ during irradiation.

In the $\text{COT}^{\cdot-}\text{K}^+\text{-COT}^-$ system, created by cation exchange, no (or little) free K^+ is present in solution. Moreover, equilibrium 4 is strongly shifted to the left for $\text{COT}^- \text{-Li}^+$. After irradiation rapid electron transfer takes place between pairs of $\text{COT}^{\cdot-}\text{K}^+$. The amount of free K^+ present is negligibly small so that $[\text{COT}^{\cdot-}\text{K}^+]$ rapidly decays to zero. Since k_2 and k_3 are both small compared to k_1 and the extent of ion pairing between COT^- and Li^+ is small as well, the free COT^- signal decays much more slowly.

From the above it is concluded that whereas the Na^+ , K^+ , and Rb^+ data can be interpreted in terms of (1), the COT^- disproportionation mechanism for the Li^+ system involves more than one reaction. The activation energy and rate constant given in Table I, therefore, merely represent *apparent* values for the disproportionation reaction. The data cannot be used to assess the role of Li^+ in the actual electron transfer.

From the data for the other systems, one can conclude that the electron transfer rate increases drastically with increasing size of the counterions. This result parallels the dependence of the rate of electron transfer between COT^- and COT^{2-} (in THF) on the cation.^{6,18} Limited data also suggest that the same counterion dependence is found for the electron transfer between an aromatic anion-cation ion pair and the neutral aromatic precursor.¹⁴

It is of some interest that a similar trend is found in outer-sphere electron transfer reactions between transition metal complexes.² Examples are the cation effect on electron transfer between MnO_4^- and MnO_4^{2-} ,³ and the anion effect on transfer between $(\text{NH}_3)_5\text{CoX}^{2+}$ and Cr^{2+} , where $\text{X} = \text{Cl}^-$ or Br^- .¹⁵

It has been proposed^{2,3,15} that the cations (or anions) act as bridging group between the electron transferring moieties. Electrostatic considerations suggest that the cations will play an important role in the formation of the activated complex by (partly) compensating for the

(13) F. J. Smentowski and G. R. Stevenson, *J. Amer. Chem. Soc.*, **91**, 7401 (1969).

(14) N. Hirota, R. Carraway, and W. Schook, *ibid.*, **90**, 3611 (1968).

(15) H. Taube, H. Myers, and B. L. Rich, *ibid.*, **75**, 4118 (1953).

electrostatic repulsion between the two anions.¹⁶ In fact, an esr study by Biloen, *et al.*,¹⁷ has shown the existence of dimers of the type $A^-Me^+A^-$ or $(A^-Me^+)_2$ in solutions of aromatic ions in MTHF. The formation of the activated complex requires desolvation of the cations. The energy required for desolvation is expected to decrease in the series Na^+ , K^+ , Rb^+ , Cs^+ ,⁴ which in part may explain the lowering of E_a (see Table I) with increasing ionic radius. Another factor (discussed in some detail in the recent review by Taube²)

(16) Note that whereas electron transfer between $A^- \cdot Me^+$ and A is slower than between A^- and A [R. L. Ward and S. I. Weissman, *J. Amer. Chem. Soc.*, **79**, 2086 (1957)], the opposite behavior is expected for transfer between two anions or an anion and dianion.

(17) P. Biloen, R. Prins, J. D. W. van Voorst, and G. J. Hooijink, *J. Chem. Phys.*, **46**, 4149 (1967).

which will affect the transfer rate is the availability of low-lying empty orbitals in the bridging group. If the metal orbitals play a role in the actual electron transfer, the energy barrier to transfer will decrease in the series Na^+ , K^+ , Rb^+ , Cs^+ . Moreover, the more extensive lowest unoccupied orbitals of the larger cations may facilitate their role as an electron conduit by increasing overlap between metal orbitals and π orbitals of the anions.

Acknowledgments. The author is grateful to the Department of Chemistry of MIT for use of their esr equipment. Helpful discussions with Dr. R. I. Gelb are gratefully acknowledged. This work was supported by a grant from the Research Corporation.

Photoinduced Electron Spin Resonance Signals in Acid-Doped Poly(*N*-vinylcarbazole)-Nitroaromatic Charge Transfer Complexes

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Contribution from the Xerox Corporation, Rochester Research Center, Webster, New York 14580. Received May 24, 1972

Abstract: A photoinduced thermally erasable esr signal has been observed in weak charge transfer complexes formed between poly(*N*-vinylcarbazole) (PVCz) and nitroaromatic acceptors such as *o*-dinitrobenzene (DNB) in the presence of strong Brønsted acids such as trichloroacetic acid (TCAA). The time, temperature, and light dependence of the esr signal intensity are found to parallel the electrical conductivity in these systems. The esr signal is attributed to the reversible formation of a protonated nitroaromatic radical anion, *i.e.*, $Ar-NO_2 \cdot H$, and the electrical conductivity to the simultaneous formation of the mobile positive charge on the radical cation of carbazole. An analysis of the kinetics of these systems shows that the formation of the conductive state occurs *via* a bimolecular reaction between an excited state of the carbazole-nitroaromatic charge transfer complex and a proton. The growth of the esr signal is described over a large time range by $\tanh \beta t$, where β is proportional to the square root of the light intensity, but at short times the growth is much faster. The decay of the signal in the dark follows a second-order rate law. The kinetic model predicts a quadratic growth curve at short times changing into a hyperbolic tangent growth at longer times as well as a bimolecular decay of the conductive state in the dark. Undesirable side reactions accompanied by a discoloration of the materials are accelerated with cyclic light exposure and heating but also occur in the dark and are at least partially attributable to the oxidation of the carbazole ring in the presence of acid. The understanding of the fundamental photo and thermal processes in these materials provides a basis for finding new photoelectric memory effects in organic polymeric solids. These processes constitute a new set of reactions in charge transfer and ion radical chemistry.

Several examples of photoinduced esr signals resulting from irradiation in the charge transfer (CT) absorption band have been reported in the literature. Ilten and Calvin¹ have reported the observation of a reversible photoinduced esr signal and photoconductivity when a solution of tetracyanoethylene (TCNE) in tetrahydrofuran (THF) was irradiated in its CT band. The simultaneous occurrences were attributed to dissociation of the charge transfer triplet state. Recombination of the donor cation radical and acceptor anion radical accounts for loss of the esr signal intensity as well as decay of the photocurrent. Stewart and Eisner² observed both a thermal and photoinduced esr signal for TCNE with dimethyl sulfoxide, *N,N*-dimethylacetamide, acetone, and THF. Once again

the esr signal arises from dissociation of the triplet state in solution, but if the enthalpy of complex formation is sufficiently large the triplet state of the complex will be appreciably populated thermally during complex formation. ESR spectra have also been observed in connection with phosphorescence from CT triplet states. Hayashi, *et al.*,³ have observed $\Delta M = 2$ transitions for the durene-tetracyanobenzene CT complex triplet state when irradiated in the CT band. A number of other very strong donor acceptor pairs have also been shown to exhibit esr spectra resulting from complete electron transfer and subsequent thermal dissociation of the complex into radical cations and anions in the solid and liquid state.⁴⁻⁶ The esr signals were

(1) D. F. Ilten and M. Calvin, *J. Chem. Phys.*, **42**, 3760 (1965).

(2) F. Stewart and M. Eisner, *Mol. Phys.*, **12**, 183 (1967).

(3) H. Hayashi, S. Nakagura, and S. I. Iwata, *ibid.*, **13**, 489 (1967).

(4) D. W. Stamires and J. Turkevich, *J. Amer. Chem. Soc.*, **85**, 2557 (1963).