Appendix

Using the symbols employed previously, for a single-component system

$$-f\mathrm{d}[\mathrm{RH}]/\mathrm{d}t = k_{\mathrm{p}}[\mathrm{ROO}\cdot][\mathrm{RH}] \qquad (27)$$

and, since the rate of formation of hydroperoxide is $-n\mathrm{d}[\mathrm{RH}]/\mathrm{d}t$, at its steady state

$$-n\mathrm{d}[\mathrm{RH}]/\mathrm{d}t = 2k_{\mathrm{t}}[\mathrm{ROO}\cdot]^2 \qquad (28)$$

Eliminating $[\mathrm{ROO}\cdot]$ gives

$$-\mathrm{d}[\mathrm{RH}]/\mathrm{d}t = nk_{\mathrm{p}}{}^2[\mathrm{RH}]^2/2fk_{\mathrm{t}} \qquad (16)$$

For a cooxidation the same over-all expression applies and can conveniently be written as

$$\frac{-\mathrm{d}([\mathrm{R_1H}] + [\mathrm{R_2H}])}{\mathrm{d}t} = \frac{nk_{\mathrm{p1}}{}^2[\mathrm{R_1H}]^2(1 + r)^2}{2fk_{\mathrm{t}}} \qquad (29)$$

This rate expression may be partitioned into fractions $1 - f$ and f involving nonperoxy and peroxy radical paths, and expressed as

$$\frac{-\mathrm{d}([\mathrm{R_1H}] + [\mathrm{R_2H}])}{\mathrm{d}t} = \frac{nk_{\mathrm{p1}}{}^2[\mathrm{R_1H}]^2(1 + r)^2}{2k_{\mathrm{t}}}\left(\frac{1 - f}{f} + 1\right) \qquad (30)$$

The rate of disappearance of $\mathrm{R_1H}$ is obtained by multiplying each of the parts by the fraction of that radical attack which involves $\mathrm{R_1H}$, *e.g.*, for peroxy radicals, $k_{\mathrm{p1}}[\mathrm{R_1H}]/(k_{\mathrm{p1}}[\mathrm{R_1H}] + k_{\mathrm{p2}}[\mathrm{R_1H}])$, giving, in terms of r and α

$$\frac{-\mathrm{d}[\mathrm{R_1H}]}{\mathrm{d}t} = \frac{nk_{\mathrm{p1}}{}^2[\mathrm{R_1H}]^2}{2k_{\mathrm{t}}} \times (1 + r)^2\left(\frac{1 - f}{f}\frac{1}{1 + \alpha r} + \frac{1}{1 + r}\right) \qquad (20)$$

Similarly

$$\frac{-\mathrm{d}[\mathrm{R_2H}]}{\mathrm{d}t} = \frac{nk_{\mathrm{p}}{}^2[\mathrm{R_1H}]^2}{2k_{\mathrm{t}}} \times (1 + r)^2\frac{1 - f}{f}\frac{\alpha r}{1 + \alpha r} + \frac{r}{1 + r} \qquad (31)$$

Dividing (31) by (20) yields (21). Obviously the treatment may be easily generalized to any number of components or carrier radicals.

Oxidation of Dicarbanions by Electron Transfer to Aromatic Acceptors

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Abstract: Aromatic hydrocarbons may oxidize dimeric dicarbanions derived from 1,1-diphenylethylene (D) or α-methylstyrene (α). These dimers have similar structures, *viz.* $\mathrm{Na^+,\bar{C}(Ph)_2CH_2CH_2\bar{C}(Ph)_2,Na^+} = {}^-\mathrm{DD}^-$ and $\mathrm{K^+,\bar{C}(CH_3)(Ph)CH_2CH_2\bar{C}(CH_3)(Ph),K^+} = {}^-\alpha\alpha^-$. In our studies the oxidation was accomplished by the following electron acceptors: anthracene (A), dimethylanthracene (DMA), pyrene (π), benzpyrene ($\mathrm{B}\pi$), and perylene radical anion ($\mathrm{Pe}\cdot^-$). The mechanism of oxidation shows some unifying features for all the investigated systems. The unimolecular dissociation of dimeric radical ions, namely, ${}^-\mathrm{DD}\cdot \rightarrow \mathrm{D}\cdot^- + \mathrm{D}$ (k_3) or ${}^-\alpha\alpha\cdot \rightarrow \alpha\cdot^- + \alpha$ ($k_{3'}$), is rate determining for all these processes and drives forward the over-all reaction. The dimeric radical ions are present in minute stationary concentrations maintained by the equilibria such as ${}^-\mathrm{DD}^- + \mathrm{A} \rightleftarrows {}^-\mathrm{DD}\cdot + \mathrm{A}\cdot^-$. This accounts for the autoinhibition of the oxidation. The above scheme accounts also for the exchange between ${}^-\mathrm{DD}^-$ and its monomer, D, although no bulk reaction takes place between these reagents. The formation of ${}^-\alpha\alpha\cdot$ is somewhat different from that of ${}^-\mathrm{DD}\cdot$. Instead of a direct electron transfer, *e.g.*, ${}^-\mathrm{DD}^- + \mathrm{A} \rightarrow {}^-\mathrm{DD}\cdot + \mathrm{A}\cdot^-$, the process occurs through the formation of an intermediate adduct, *i.e.*, ${}^-\alpha\alpha\text{–}\mathrm{A}^-$ followed by ${}^-\alpha\alpha\text{–}\mathrm{A}^- \rightarrow {}^-\alpha\alpha\cdot + \mathrm{A}\cdot^-$. The factors favoring the indirect electron transfer are discussed. Diadduct, *e.g.*, ${}^-\mathrm{A}\alpha\alpha\text{–}\mathrm{A}^-$, is formed as well as the monoadduct. The contribution of the latter to the over-all oxidation is negligible, and consequently its formation, favored by higher initial concentration of the acceptor, accounts for the most peculiar behavior of the system. Whereas the oxidation is accelerated by increase in the acceptor's concentration when its concentration is relatively low, the reaction is retarded by the acceptor when its initial concentration of the acceptor is sufficiently large.

Carbanions may be oxidized by suitable electron acceptors. For example, at the beginning of this century Schlenk described the reaction[1]

$$\mathrm{Ph_3C^-} + \text{anthracene (A)} \rightleftarrows \mathrm{Ph_3C}\cdot + \text{anthracene}\cdot^-\ (\mathrm{A}\cdot^-)$$

in which the electron-transfer process oxidizes a carbanion to its parent radical and reduces an aromatic hydrocarbon to its radical anion. In the following years similar reactions were reported by other investigators.

Quantitative studies of the kinetics of electron transfers from some dicarbanions to aromatic acceptors were carried out in our laboratory during the last

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(1) W. Schlenk and R. Ochs, *Ber.*, 49, 608 (1916).

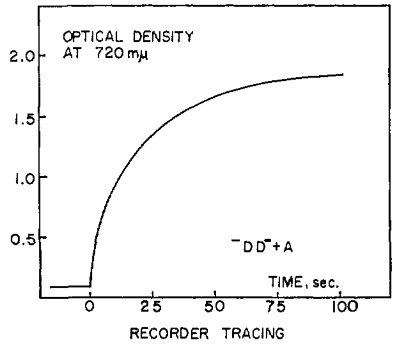

Figure 1. The course of the oxidation $^-DD^- + A \rightarrow$ products; determined by the increase of optical density at 720 mμ (λ_{max} of $A\cdot^-$) as a function of time. Note the pronounced autoinhibition within about 50 sec.

few years, and the results of these investigations are reviewed in the present paper. The investigated dicarbanions are formed when a solution of 1,1-diphenylethylene (D) or α-methylstyrene (α) in tetrahydrofuran, or in other suitable ethereal solvent, is contacted with alkali metal. In our studies sodium was used in the preparation of the dimeric dianions of D, and potassium in studies involving α-methylstyrene. Eventually, all the hydrocarbon is converted into the desired dimer, *viz.*

$$\bar{C}(Ph)_2CH_2CH_2\bar{C}(Ph)_2 = {}^-DD^-$$

is formed from D, and

$$\bar{C}(CH_3)(Ph)CH_2CH_2\bar{C}(CH_3)(Ph) = {}^-\alpha\alpha^-$$

is produced from α. The resulting dicarbanions are stable in aprotic solvents.

Although the abbreviated notations $^-DD^-$ and $^-\alpha\alpha^-$ often will be used in this paper, it needs to be stressed that in tetrahydrofuran, and in other ethereal solvents, these dianions exist mainly as ion pairs. Thus, in our studies we dealt with $Na^+,{}^-DD^-,Na^+$ and $K^+,{}^-\alpha\alpha^-,K^+$. Moreover, the resulting radical ions also are present mainly as ion pairs.

Oxidation of $^-DD^-$ by Aromatic Hydrocarbons

The dimeric dianions $^-DD^-$ readily react with anthracene (A), pyrene (π), and 9,10-dimethylanthracene (DMA). The oxidation proceeds until equilibria such as

$$Na^+,{}^-DD^-,Na^+ + 2A \rightleftharpoons 2D + 2A\cdot^-,Na^+ \qquad (1)$$

are established. For example, quantitative studies[2] showed that for the sodium salts in tetrahydrofuran solution the relevant equilibrium constant, K_1, is 0.11 *M* at 28°, and ΔH_1 and ΔS_1 are 5.0 kcal/mole and 12 eu, respectively. The final equilibria are slowly established; it takes a few days to reach the ultimate state of equilibrium.

The kinetics of the oxidation was studied spectrophotometrically in a stopped-flow system by following the decay of the absorption peak of $^-DD^-$ (λ_{max} 470 mμ) or the appearance of the absorption peak of the aromatic radical anions (λ_{max} 725 mμ for $A\cdot^-$ or $DMA\cdot^-$ and 730 mμ for $\pi\cdot^-$. The complete absorption spectra of these radical ions show additional peaks which were reported elsewhere.[3,4]

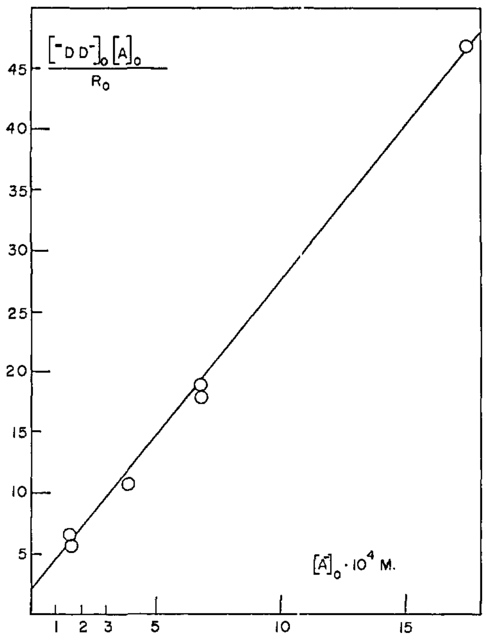

Figure 2. Plot of $\{(d[A\cdot^-]/dt)/[^-DD^-][\text{aromatic}]\}^{-1}$ *vs.* [aromatic·⁻]. The slope gives $1/2k_3K_2$ (solvent THF, 25°).

The course of the reaction observed during the first few minutes after stopping the flow is exemplified by Figure 1. Although the system is far from its equilibrium (the latter is attained only after a few days), the conversion becomes extremely slow after a few minutes. This is a most interesting and significant feature of these processes, and it indicates that some products of the reaction act as retarders. Indeed, it was established that the addition of the relevant radical anions ($A\cdot^-$, $\pi\cdot^-$, or $DMA\cdot^-$, respectively) pronouncedly slows down the observed process.

The rate of the reaction was found to be proportional to the concentration of $^-DD^-$ and of the aromatic hydrocarbon which acts as an electron acceptor, and to be invertially proportional to the concentration of the resulting radical ion. Thus, a plot of the $\{\text{rate}/[^-DD^-][\text{aromatic}]\}^{-1}$ *vs.* [aromatic·⁻] is linear, as seen from Figure 2. The initial concentration of the radical ions was varied by adding it to the parent hydrocarbon.

Alternatively, the proposed kinetic law was tested by plotting its integrated form, *viz.*

$$\int_{x_1}^{x_2} x\mathrm{d}x \bigg/ \left\{[^-DD^-]_0 - \frac{1}{2}x\right\}\{[\text{aromatic}]_0 - x\}$$

vs. $t_2 - t_1$. Here x denotes the momentary concentration of the relevant radical ion, x_1 and x_2 are its concentrations at times t_1 and t_2, and the calculation was performed by using the experimental curves, such as the one shown in Figure 1, integrating the results from t_1 of about a few seconds up to any desired time t_2. For the sake of illustration, plots of such integrals, derived from the experiments performed with anthracene and pyrene, respectively, are shown in Figure 3.

The kinetic results suggest the following mechanism of the over-all oxidation. A bimolecular reversible electron transfer (2) initiates the over-all process, *viz.*

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[2] J. Jagur-Grodzinski, M. Levy, M. Feld, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 2168 (1962).

[3] D. Gill, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **60**, 1424 (1964).

[4] P. Bald, G. J. Hoijtink, and J. W. H. Schreurns, *Rec. Trav. Chim.*, **76**, 813 (1957).

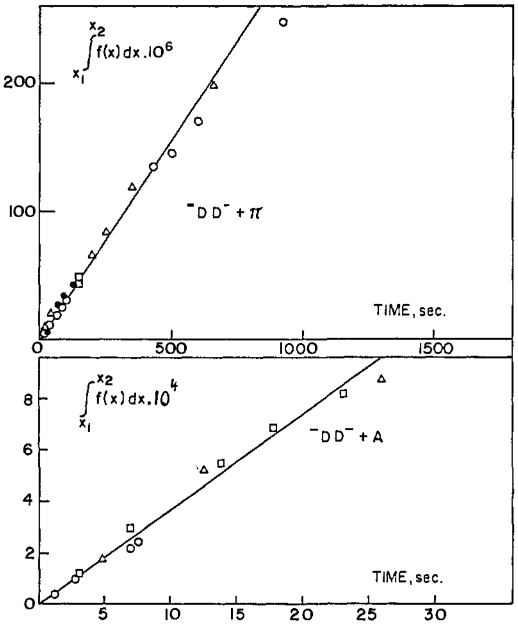

Figure 3. Plot of the integral $\int_{x_1}^{x_2} x\mathrm{d}x/\{[^-DD^-]_0 - {}^1/_2x\}\{[\text{aromatic}]_0 - x\}$ *vs.* $t_2 - t_1 = \Delta t$: upper part, $^-DD^- + \pi$; lower part, $^-DD^- + A$. Points of different shape refer to different experiments performed at different initial conditions. The slope gives $2k_3K_2$ (solvent THF, 25°).

$$^-DD^- + \text{aromatic} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} {}^-DD\cdot + \text{aromatic}\cdot^- \qquad K_{2.\text{aromatic}} \quad (2)$$

Unpublished results from this laboratory allowed us to estimate K_2 for the pyrene system, *viz.*, $K_{2\pi} \approx 10^{-7}$. Since the electron transfer equilibrium constants $\pi\cdot^- + A \rightleftharpoons \pi + A\cdot^-$ and $\pi\cdot^- + DMA \rightleftharpoons \pi + DMA\cdot^-$ are about 100, K_{2A} and K_{2DMA} should be of the order of 10^{-5}; *i.e.*, for all the investigated systems equilibrium 2 favors the left-hand side of the equation. The concentration of the dimeric radical ion, $^-DD\cdot$, would, therefore, be minute, and we assume that this intermediate spontaneously dissociates, *viz.*

$$^-DD\cdot \xrightarrow{k_3} D\cdot^- + D \qquad (3)$$

Reaction 3 is considered to be the rate-determining step of the over-all oxidation which is completed by the rapid electron transfer

$$D\cdot^- + \text{aromatic} \xrightarrow{k_4} D + \text{aromatic}\cdot^- \qquad (4)$$

A remark is not out of place. Electron-transfer 2 forms a proper radical from a carbanion and converts aromatic hydrocarbon into its radical ion. It is not surprising, therefore, that this step is endothermic and, as will be seen soon, k_2 relatively low. Reaction 4 converts one radical anion into another, and since the electron affinities of anthracene, pyrene, and 9,10-dimethylanthracene are substantially larger than that of 1,1-diphenylethylene,[5,6] k_4 is expected to be about $10^8\ M^{-1}\ \text{sec}^{-1}$.

The proposed mechanism leads to the following rate equation, if the stationary state assumption for $^-DD\cdot$ is valid.

$$\text{rate} = \mathrm{d}[\text{aromatic}\cdot^-]/\mathrm{d}t = 2k_3k_2[^-DD^-][\text{aromatic}]/\{k_3 + k_{-2}[\text{aromatic}\cdot^-]\}$$

It seems that a sufficient amount of radical ions is formed in about the first few seconds to make reaction −2 much faster than 3, *i.e.*, k_{-2} [aromatic·⁻] $\gg k_3$. Thereafter, the rate of oxidation is given by the simplified equation, *viz.*

$$\text{rate} = 2k_3K_2[^-DD^-][\text{aromatic}]/[\text{aromatic}\cdot^-]$$

and this expression was used for the integration of the results shown in Figure 3. In fact, experiments performed at extremely low anthracene concentrations[3] demonstrated that for the system $k_3/k_{-2} < 10^{-7}\ M$, and this ratio seems to be even lower for the systems involving pyrene or dimethylanthracene.

The results of the integration or the effects of retardation due to the addition of the relevant radical ions permit us to calculate the composite constants, namely, k_3K_2's. Step 3 of the proposed mechanism is common for all the investigated reactions, *i.e.*, for those involving anthracene, or pyrene, or dimethylanthracene. Therefore, the kinetic results provide us with the ratios $K_{2(A)}/K_{2(\pi)}$ and $K_{2(DMA)}/K_{2(\pi)}$ where

$$^-DD^- + A \rightleftarrows {}^-DD\cdot + A\cdot^- \qquad K_{2(A)}$$

$$^-DD^- + \pi \rightleftarrows {}^-DD\cdot + \pi\cdot^- \qquad K_{2(\pi)}$$

$$^-DD^- + DMA \rightleftarrows {}^-DD\cdot + DMA\cdot^- \qquad K_{2(DMA)}$$

However, these ratios are equal to the equilibrium constants of the electron-transfer reactions

$$A + \pi\cdot^- \rightleftarrows A\cdot^- + \pi \qquad K_{A,\pi}$$

and

$$DMA + \pi\cdot^- \rightleftarrows DMA\cdot^- + \pi \qquad K_{DMA,\pi}$$

namely $K_{2(A)}/K_{2(\pi)} = K_{A,\pi}$ and $K_{2(DMA)}/K_{2(\pi)} = K_{DMA,\pi}$. Because the latter were determined directly by spectrophotometric studies,[3] the reliability of the proposed mechanism could be tested. The available results are collected in Table I and show remarkable agreement between the kinetic and thermodynamic findings. This is, therefore, strong evidence in favor of the assumed kinetic scheme, and it indicates that reaction 3 is indeed the common rate-determining step of all these processes.

Table I

System $Na^+,{}^-DD^-,Na^+ + \text{aromatic} \overset{k_2}{\rightleftarrows} Na^+,{}^-DD\cdot + \text{aromatic}\cdot^-,Na^+\ (K_2)$

$$Na^+,{}^-DD\cdot \xrightarrow{k_3} Na^+,\dot{D}\cdot^- + D^a$$

Aromatic	k_2, M^{-1} sec$^{-1\,b}$	$2k_3K_2$, sec$^{-1\,b}$
Anthracene (A)	1	$(3.8) \times 10^{-5}$
Pyrene (π)		$(3.2 \pm 0.1) \times 10^{-7}$
9,10-Dimethylanthracene (DMA)		$(4.3 \pm 0.3) \times 10^{-5}$

Comparison between Kinetic and Thermodynamic Data[c]

$2k_3K_{2\pi}/2k_3K_{2A} = K_{\pi.A}$	$K_{\pi,A}$(spectrophotometric)
0.85×10^{-2}	0.9×10^{-2}
$2k_3K_{2\pi}/2k_3K_{2DMA}$	$K_{\pi.DMA}$(spectrophotometric)
0.75×10^{-2}	1.1×10^{-2}

[a] Solvent THF, 25°. [b] Values from ref 2 and 3. [c] Reference 3.

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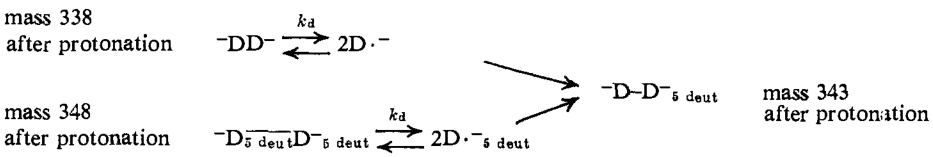
(5) (a) S. Wawzonek and T. Wang-Fan, *J. Am. Chem. Soc.*, **68**, 2541 (1946); (b) S. Wawzonek and H. A. Laitinen, *ibid.*, **64**, 2365 (1942).

(6) J. Jagur-Grodzinski and M. Szwarc, *Proc. Roy. Soc.* (London), **288**, 224 (1965).

Scheme I



The above mechanism accounts also for the exchange taking place between $^-DD^-$ and D.[7] Addition of 1,1-diphenylethylene (D) to a solution of $^-DD^-$ does not lead to any net reaction. The large steric strain arising from the presence of four bulky phenyl groups on two carbon atoms separated by a CH_2 group prevents the formation of trimers, tetramers, or polymers, and therefore diphenylethylene remains inert in such a solution. Nevertheless, the experiments performed with radioactive D and nonactive $^-DD^-$, or *vice versa*, demonstrate that the radioactivity is gradually incorporated in the dimer.

A direct reaction, *viz.*

$$D^{14} + {}^-D\cdot D^- \longrightarrow D + {}^-D^{14}\cdot D^-$$

is implausible. However, the following two plausible routes may account for the observed exchange, namely

$$^-DD^- \underset{k_a}{\overset{k_d}{\rightleftarrows}} 2D\cdot^- \qquad (5)$$

followed by

$$D\cdot^- + D^{14} \rightleftarrows D + (D^{14})\cdot^- \qquad (6)$$

or

$$^-DD^- + D \rightleftarrows {}^-DD\cdot + D\cdot^- \qquad (7)$$

followed by the decomposition of $^-DD\cdot$, *i.e.*

$$^-DD\cdot \rightleftarrows D\cdot^- + D \qquad (3)$$

and eventually by exchange (6).

The first alternative leads to the rate of exchange, R_{ex}, given by the equation

$$R_{ex} = 2k_d[^-DD^-]$$

i.e., R_{ex} would be determined only by the rate of dissociation of $^-DD^-$, because reaction 6 certainly is very fast. The second alternative demands that

$$R_{ex} = 2_{k-3}(K_5)^{1/2}[D][^-DD^-]^{1/2}$$

because the equilibrium concentrations of the monomeric $D\cdot^-$ radical ions and of the dimeric $^-DD\cdot$ radicals are extremely low as shown by the esr studies;[8] only an extremely weak signal was observed from concentrated solutions of $^-DD^-$ containing a large excess of D.

Reaction 7 could be the rate-determining step of the exchange if $k_7[^-DD^-][D] \ll k_3[^-DD\cdot]$. Had this been the case, then

$$R_{ex} = k_7[D][^-DD^-]$$

Experiments performed for a wide range of $^-DD^-$ concentration (from 1 to 8 × 10^{-2} *M*) demonstrated that the rate of exchange increases as square root of its concentration.[7] Consequently, $k_7[^-DD^-][D] \gg k_3[^-DD\cdot]$ and therefore the exchange had to be governed by reaction 3. This is seen from inspection of Figure 4. The plot of $R_{ex}/[^-DD^-]$ is linear with the ratio $[D]/[^-DD^-]^{1/2}$, the slope of the line gives $2_{k-3}(K_5)^{1/2}$, and the intercept provides the value of $2k_d$. The latter is experimentally indistinguishable from 0, *i.e.*, $k_d < 10^{-7}$ sec^{-1}. Nevertheless, this constant eventually was determined[9] by studying the exchange between an ordinary $^-DD^-$ and $^-DD^-$ containing five deuterium atoms in *each* monomer. The rate of dissociation was measured by the rate of formation of the mixed $^-DD^-$ dimer containing five deuterium atoms per dimer, as shown in Scheme I, and its fraction in the protonated products was determined by mass spectrography. This study led to $k_d \approx 10^{-9}$ sec^{-1}.

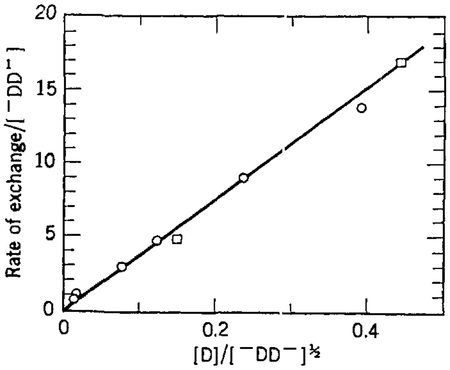


Figure 4. Rate of exchange, R_{ex}, between $^-DD^-$ and radioactive D, plotted as $R_{ex}/[^-DD^-]$ *vs.* $[D]/[^-DD^-]^{1/2}$. The slopes give $k_{-3}K_5^{1/2} = 25 \times 10^{-6}\ M^{-1/2}$ sec^{-1} at 25° in THF.

The rate of association of $D\cdot^-$ radical ions in tetrahydrofuran was determined directly,[11] using a flow technique, and the results led to k_a of about 1–2 × 10^6 M^{-1} sec^{-1}.

$$2D\cdot^-,Na^+ \xrightarrow{k_a} Na^+,{}^-DD^-,Na^+$$

Hence, the equilibrium constant, K_5, of $^-DD^-$ dissociation is about 10^{-15} *M*. The kinetics of exchange between $^-DD^-$ and D provides us with the composite constant $k_{-3}K_5^{1/2} = 25 \times 10^{-6}\ M^{-1/2}$ sec^{-1} at about 25°. The absolute value of the rate constant of combination, k_{-3}, of $D\cdot^-$ and D into $^-DD\cdot$ is therefore about 800 sec^{-1}. The rate constant, k_3, of the reverse process, $^-DD\cdot \rightarrow D\cdot^- + D$, was calculated by combining the directly determined value of k_3K_2 with the value K_2 determined indirectly (see above). Thus, k_3 is found to be about 1 sec^{-1}.

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[7] G. Spach, H. Monteiro, M. Levy, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 1809 (1962).

[8] Unpublished results from this laboratory.

[9] N. Ogata, unpublished results from this laboratory; see also ref 10.

[10] M. Szwarc and R. Asami, *J. Am. Chem. Soc.*, **84**, 2269 (1962).

[11] M. Matsuda, J. Jagur-Grodzinski, and M. Szwarc, *Proc. Roy. Soc.* (London), **A288**, 212 (1965).

The kinetics discussed in the preceding paragraphs refers to those stages of the over-all process in which the concentration of the intermediate dimeric radicals, $^{-}\mathrm{DD}\cdot$, attains its equilibrium value determined by reaction 2. A study of the very initial stage of the process permits us to determine k_2, the rate constant of the electron transfer from $^{-}\mathrm{DD}^{-}$ to the aromatic acceptor. This was done for the anthracene system[12] only, and k_2 was found to be about 1 M^{-1} sec^{-1}. There is an indication that in the pyrene system k_2 is substantially lower; equilibrium 2 is established in this system in about 30 sec, while in the anthracene system it is attained within 2–3 sec.

The work described here demonstrates that the oxidation of $^{-}\mathrm{DD}^{-}$ by aromatic hydrocarbons involves the direct electron-transfer equilibrium 2, followed by the spontaneous decomposition of the dimeric radical anion, $^{-}\mathrm{DD}\cdot$

$$\mathrm{Na}^+,^{-}\mathrm{DD}\cdot \xrightarrow{k_3} \mathrm{Na}^+,\mathrm{D}\cdot^- + \mathrm{D} \qquad (3)$$

Participation of this species in the over-all reaction seems to be undeniable. However, an interesting question arises as to why an electron-transfer reaction

$$\mathrm{Na}^+,^{-}\mathrm{DD}\cdot + \text{aromatic} \longrightarrow 2\mathrm{D} + \mathrm{Na}^+,\text{aromatic}\cdot^- \qquad (8)$$

does not compete with the unimolecular dissociation of $\mathrm{Na}^+,^{-}\mathrm{DD}\cdot$. It seems that reaction 2 is enhanced by the proximity of two negatively charged end groups. The repulsion between them contributes to the driving force of the electron transfer. This gain is not available when $^{-}\mathrm{DD}\cdot$ interacts with the acceptor, and thus the rate of (8) should be much lower than that of (2). It was previously pointed out that for the anthracene system $k_2 \approx 1$ M^{-1} sec^{-1}. Because the concentration of A is less than 10^{-1} and $k_8 \ll k_2$, one concludes that $k_8[\mathrm{A}] < k_3$ because $k_3 \approx 1$ sec^{-1}. On the other hand, k_{-2} was calculated to be 10^5 M^{-1} sec^{-1}, and therefore equilibrium 2 is established even for $[\mathrm{A}\cdot^-]$ as low as 10^{-5} M.

The situation may be reversed if the reaction involves acceptors of very high electron affinity. For example, the oxidation of $^{-}\mathrm{DD}^{-}$ by perylene is completed in less than 0.1 sec. In this process $^{-}\mathrm{DD}\cdot$ probably rapidly reacts with this powerful electron acceptor because the half-life time of the unimolecular decomposition of $^{-}\mathrm{DD}\cdot$ is about 1 sec; *i.e.*, this dissociation is too slow to account for the observed rate.

For the sake of the reader's convenience, the kinetic constants pertaining to all these systems are collected in Table II.

Table II. Summary of Reactions Participating in the Oxidation of $^{-}\mathrm{DD}\cdot^{-}$ [a]

$^{-}\mathrm{DD}^{-} \underset{k_a}{\overset{k_d}{\rightleftarrows}} 2\mathrm{D}\cdot^-$	$K_5 \approx 10^{-15}$ M
$k_a = 1\text{–}2 \times 10^6$ M^{-1} sec^{-1}	$k_d \approx 10^{-9}$ sec^{-1}
$^{-}\mathrm{DD}\cdot \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{D}\cdot^- + \mathrm{D}$	$K_3 \approx 10^{-3}$ M
$k_3 \approx 1$ sec^{-1}	$k_{-3} = 800$ M^{-1} sec^{-1}

[a] Solvent THF, 25°; counterion, Na$^+$.

Oxidation of $^{-}\alpha\alpha^{-}$ by Aromatic Acceptors

Powerful acceptors react with the dimeric dianions of α-methylstyrene, $^{-}\alpha\alpha^{-}$, in the same way as with $^{-}\mathrm{DD}^{-}$. The oxidation by perylene or phenazine is completed in less than 0.1 sec, the electron acceptor being quantitatively converted into the corresponding radical ion. Presumably, $^{-}\alpha\alpha\cdot$, as well as $^{-}\alpha\alpha^{-}$, is involved in the electron-transfer process, *i.e.*

$$^{-}\alpha\alpha\cdot + \text{perylene} \longrightarrow 2\alpha + \text{perylene}\cdot^-$$

The less powerful acceptor perylene$\cdot^-$ radical ion reacts with $^{-}\alpha\alpha^{-}$ as does anthracene with $^{-}\mathrm{DD}^{-}$. Kinetic studies[13] showed that the reaction is retarded by the perylene dianion, Pe^{2-}, and the results conform with the previously discussed scheme, *i.e.*

$$\mathrm{K}^+,^{-}\alpha\alpha^{-},\mathrm{K}^+ + \mathrm{Pe}\cdot^-,\mathrm{K} \rightleftarrows \mathrm{K}^+,^{-}\alpha\alpha\cdot + \mathrm{Pe}^{2-},2\mathrm{K}^+ \qquad K'_{2\mathrm{Pe}\cdot^-}$$

$$\mathrm{K}^+,^{-}\alpha\alpha\cdot \xrightarrow{k_{3'}} \mathrm{K}^+,\alpha\cdot^- + \alpha \qquad \text{rate-determining step}$$

and

$$\mathrm{K}^+,\alpha\cdot^- + \mathrm{Pe}\cdot^-,\mathrm{K}^+ \longrightarrow \alpha + \mathrm{Pe}^{2-},2\mathrm{K}^+$$

Quantitative treatment of the data give $2k_{3'}\,K'_{2\mathrm{Pe}\cdot^-} = 13 \times 10^{-2}$ sec^{-1}.

In all the reactions discussed up to now, the electron transfer seems to take place through a direct bimolecular collision; no evidence was provided for the formation of an intermediate transient adduct. The adducts were observed, however, in the oxidation of $^{-}\alpha\alpha^{-}$ by anthracene,[14] pyrene,[13] and benzpyrene.[15] On mixing tetrahydrofuran solutions of $\mathrm{K}^+,^{-}\alpha\alpha^{-},\mathrm{K}^+$ and anthracene, a new species, absorbing at 451 mμ, is rapidly formed. Kinetic studies performed in a flow system[16] demonstrated that the addition obeys second order kinetics and converts one molecule of anthracene and one carbanionic end of the dimer into the adduct; the bimolecular rate constant was calculated to be about 5000 M^{-1} sec^{-1}. Hence, under our experimental conditions the addition is completed within 0.2 sec.

The stoichiometry of this reaction is evident from Figure 5. For a series of experiments in which the concentration of $^{-}\alpha\alpha^{-}$ was kept constant and that of A varied, the optical density at 451 mμ was determined in about 0.2 sec after mixing the reagents. This time is sufficiently long to permit the completion of the addition but short enough to prevent any measurable decomposition of the adduct. The optical density increases linearly with the ratio $[\mathrm{A}]_0/[^{-}\alpha\alpha^{-}]_0$ as long as its value does not exceed 2. For higher ratios the optical density remains constant and is not affected by further increase of the anthracene concentration.

It is apparent that both ends of the dimer react with anthracene, the rate of addition of one end being virtually unaffected by the fate of the other. The nature of the adduct was deduced from the analysis of its spectrum which was compared with the spectra of analogous adducts and from the analysis of products of protonation. The linkage is due to the formation

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(12) T. L. Staples, unpublished results from this laboratory.

(13) S. C. Chadha, J. Jagur-Grodzinski, and M. Szwarc, *Trans. Faraday Soc.*, **65**, 1074 (1969).

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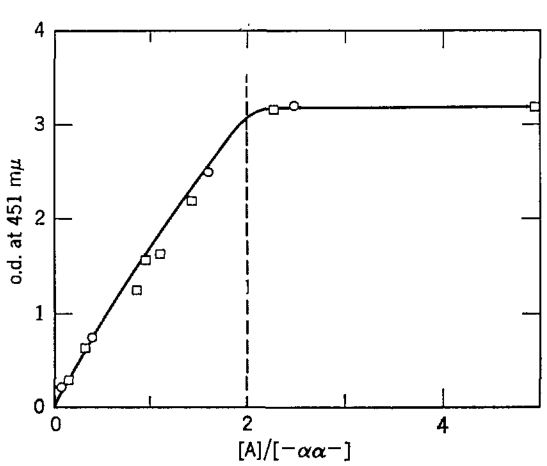


Figure 5. Optical density at 451 mμ (λ_{max} of the adduct between $^-\alpha\alpha^-$ and anthracene) at $[^-\alpha\alpha^-]_0$ = constant and variable $[A]_0$ plotted as the function of $[A]_0/[^-\alpha\alpha^-]_0$; observed in a flow system about 0.2 sec after mixing the reagents (solvent THF, 25°, counterion K^+).

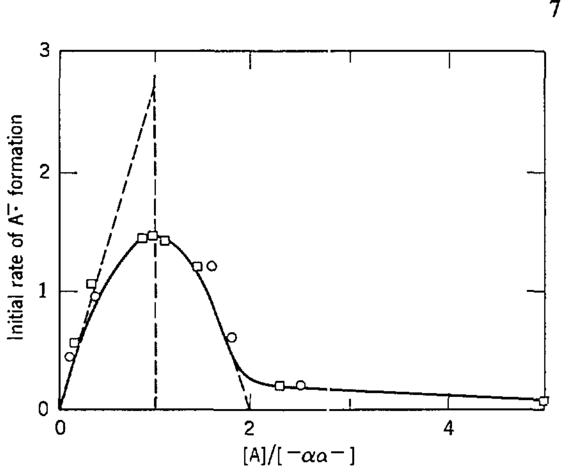
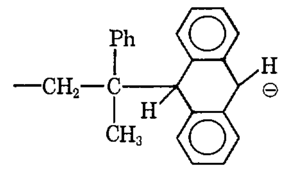


Figure 6. The rate of the initial formation of $A\cdot^-$; $R_0 = (d[A\cdot^-]/dt)_0$ plotted *vs.* $[A]_0/[^-\alpha\alpha^-]_0$ for a constant $[^-\alpha\alpha^-]_0$ (25°, solvent THF). Note the theoretical curve (parabola) and R_0 = max at $[A]_0/[^-\alpha\alpha^-]_0 = 1$. Linearly extrapolated R_0 is twice R_0(max) at $[A]_0/[^-\alpha\alpha^-]_0 = 1$.

of a covalent bond between the carbanion of $^-\alpha\alpha^-$ and the 9 carbon atom of anthracene, *i.e.*



Its spectrum verifies the conversion of carbon 10 of anthracene into a carbanionic group. Thus, the addition is represented by two independent reactions, both proceeding with closely similar rate constant, *viz.*

$$^-\alpha\alpha^- + A \longrightarrow {}^-\alpha\alpha\text{–}A^-$$

$$^-A\text{–}\alpha\alpha^- + A \longrightarrow {}^-A\text{–}\alpha\alpha\text{–}A^-$$

The adduct decomposes within a minute or two yielding $A\cdot^-$ radical ions. The progress of the reaction was followed spectrophotometrically by observing the increase of optical density at 725 mμ (λ_{max} of $A\cdot^-$). The initial rate was determined for a series of experiments performed at a constant concentration of $^-\alpha\alpha^-$ and variable concentrations of A, and the pertinent results are presented in Figure 6. The rate increases with increasing anthracene concentration, a trivial result because the amount of the adduct to be decomposed increases accordingly. However, the increase of the initial rate is not linear; it reaches its maximum value for the ratio $[A]_0/[^-\alpha\alpha^-]_0 = 1$, and thereafter its value decreases as $[A]_0$ increases. This astonishing result implies that the radical ions, $A\cdot^-$, are formed by the decomposition of $^-\alpha\alpha\text{–}A^-$, whereas the contribution of $^-A\text{–}\alpha\alpha\text{–}A^-$ to the rate is negligible due to some reasons which have to be discussed.

This conclusion may be further verified. The addition of anthracene to either end of $^-\alpha\alpha^-$ has been assumed to be irreversible, and its rate was shown to be unaffected by the fate of the other end. Hence, denoting by p the ratio $[A]_0/2[^-\alpha\alpha^-]_0$, we conclude that the proportions of $^-\alpha\alpha^-$, $^-\alpha\alpha\text{–}A^-$, and $^-A\text{–}\alpha\alpha\text{–}A^-$ formed in a mixture of A and $^-\alpha\alpha^-$ are given by $(1 - p)^2$, $2p(1 - p)$, and p^2, respectively. This was confirmed by analyzing the products of protonation of the pertinent solutions. The initial rate of decomposition for a constant $[^-\alpha\alpha^-]_0$ and variable $[A]_0$ is expected to be proportional to $2p(1 - p)$ if only $^-\alpha\alpha\text{–}A^-$ contributes to the reaction. Hence, the experimental points should fit a parabola with a maximum at $p = {}^1/_2$, *i.e.*, $[A]_0/[^-\alpha\alpha^-]_0 = 1$. This, indeed, is shown by Figure 6.

To gain further insight into the mechanism of decomposition, its kinetics was investigated. The studies were performed with mixtures containing a large excess of $^-\alpha\alpha^-$ to ascertain the formation of $^-\alpha\alpha\text{–}A^-$ with a virtual exclusion of $^-A\text{–}\alpha\alpha\text{–}A^-$. The reaction was found to be retarded by $A\cdot^-$, whether it was added initially to the reacting solution or formed in the course of the decomposition, and the rate was given by

$$d[A\cdot^-]/dt = \text{constant}\{[A]_0 - [A\cdot^-]\}/\{\beta + [A\cdot^-]\}$$

These results are accounted for by the following mechanism

$$^-\alpha\alpha\text{–}A^- \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} {}^-\alpha\alpha\cdot + A\cdot^- \qquad (9)$$

$$^-\alpha\alpha\cdot \xrightarrow{k_{3'}} \alpha\cdot^- + \alpha \qquad \text{rate determining} \qquad (3')$$

$$^-\alpha\alpha\cdot + \alpha^- \longrightarrow {}^-\alpha\alpha^- + \alpha \qquad \text{very fast}$$

which resembles the previously discussed schemes. Again, the rapid reaction −9 accounts for the retarding effect of $A\cdot^-$, and reaction 3′ becomes the rate-determining step.

Why is the decomposition of $^-A\text{–}\alpha\alpha\text{–}A^-$ slow? This may be due either to the unfavorable equilibrium

$$^-A\text{–}\alpha\alpha\text{–}A^- \longrightarrow {}^-A\text{–}\alpha\alpha\cdot + A\cdot^-$$

or, more likely, to the slowness of decomposition of $^-A\text{–}\alpha\alpha\cdot$, *viz.*

$$^-A\text{–}\alpha\alpha\cdot \xrightarrow{k_{10}} A\cdot^- + 2\alpha \qquad (10)$$

The latter reaction requires simultaneous rupture of two covalent bonds, and this may account for $k_{10} \ll k_{3'}$. Its alternative course, *viz.*, $^-A\alpha\alpha\cdot \rightarrow {}^-A\alpha\cdot + A$ followed by $^-A\alpha\cdot \rightarrow A\cdot^- + \alpha$, probably is even slower. Only the energy of *one* C═C double bond is gained in each of the above steps, while *two* double

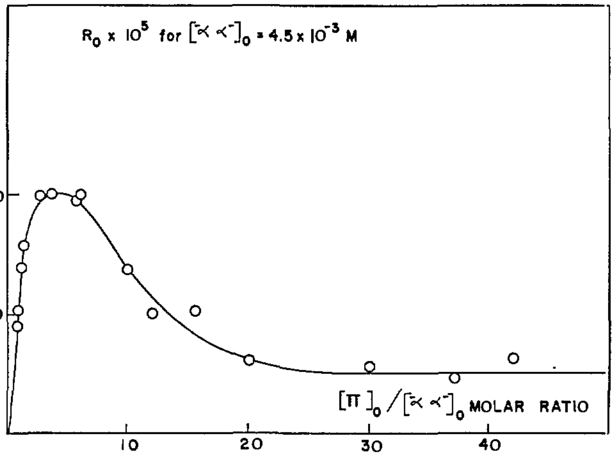


Figure 7. The rate of the initial formation of $\pi\cdot^-$; $R_0 = (d[\pi\cdot^-]/dt)_0$ plotted *vs.* $[\pi]_0/[^-\alpha\alpha^-]_0$ for a constant $[^-\alpha\alpha^-]_0$. Note R_0 = max for $[\pi]_0/[^-\alpha\alpha^-]_0$ of about 4 (25°; solvent THF, counterion K^+).

bonds are *simultaneously* formed in the decomposition of $^-\alpha\alpha\cdot$ or in reaction 10, rupturing two bonds at once.

Kinetics of $^-\alpha\alpha^-$ oxidation by anthracene is relatively simple due to the virtual irreversibility of the addition, $^-\alpha\alpha^- + A \rightarrow {}^-\alpha\alpha\text{–}A^-$, which is over in a fraction of a second. Even in the presence of a small excess of $^-\alpha\alpha^-$, essentially all the anthracene is bounded because the equilibrium constant of the addition is larger than $10^5\ M^{-1}$. The addition of pyrene (π) is less favorable, and the equilibrium constant, K_{11}

$$^-\alpha\alpha^- + \pi \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} {}^-\alpha\alpha\text{–}\pi^- \tag{11}$$

was determined[13] to be 120 M^{-1} only. Consequently, a substantial fraction of the acceptor remains free when $^-\alpha\alpha^-$ is oxidized by pyrene, although equilibrium 11 is established rapidly. The addition of a second molecule of pyrene, *i.e.*

$$^-\pi\text{–}\alpha\alpha^- + \pi \longrightarrow {}^-\pi\text{–}\alpha\alpha\text{–}\pi^- \tag{12}$$

is still less favorable.

In spite of this, the oxidation by pyrene shows some features resembling those observed for the anthracene system. For a constant $[^-\alpha\alpha^-]_0$ the initial rate, R_0, of the $\pi\cdot^-$ radical-ion formation increases with increasing $[\pi]_0$, but at a sufficiently high concentration of pyrene it reaches its maximum, and then the rate decreases as $[\pi]_0$ increases still further. This is seen in Figure 7, and such a behavior again indicates that the decomposition of $^-\pi\text{–}\alpha\alpha\text{–}\pi^-$ is slow while that of $^-\alpha\alpha\text{–}\pi^-$ is rapid. The relatively low values of K_{11} and K_{12} are responsible for the larger values of the ratio $[\pi]_0/[^-\alpha\alpha^-]_0$ at which R_0 reaches its maximum rate. Furthermore, the magnitude of this ratio depends now on $[^-\alpha\alpha^-]_0$. Thus, this system differs from that involving anthracene, only in some details; in the latter R_0 is at maximum when $[A]_0/[^-\alpha\alpha^-]_0 = 1$, whatever the initial concentration of $^-\alpha\alpha^-$. Kinetic study[13] of the $^-\alpha\alpha^- + \pi$ system again shows that $\pi\cdot^-$ is formed by two steps: the reversible dissociation

$$^-\alpha\alpha\text{–}\pi^- \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} {}^-\alpha\alpha\cdot + \pi\cdot^- \tag{13}$$

favoring the adduct, and the decomposition

$$^-\alpha\alpha\cdot \xrightarrow{k_{3'}} \alpha\cdot^- + \alpha \tag{3'}$$

which is responsible for the progress of the over-all reaction.

The retarding effect of $\pi\cdot^-$ upon its rate of formation provides the evidence for (13). A direct bimolecular reaction

$$^-\alpha\alpha^- + \pi \longrightarrow {}^-\alpha\alpha\cdot + \pi\cdot^-$$

does not seem to be significant. Although the initial rate of oxidation, R_0, increases with $[^-\alpha\alpha^-]_0$ at constant concentration of $[\pi]_0$, eventually it becomes constant when $[^-\alpha\alpha^-]_0$ is sufficiently large. This can be accounted for by reaction 11 followed by 13; a large excess of $[^-\alpha\alpha^-]_0$ converts *all* π into $^-\alpha\alpha\text{–}\pi^-$ and thereafter the rate of oxidation is not affected by further increase of $[^-\alpha\alpha^-]_0$. On the other hand, the reaction $^-\alpha\alpha^- + \pi \rightleftharpoons {}^-\alpha\alpha\cdot + \pi\cdot^-$ cannot account for the rate-leveling effect.

Assuming that the rate constant, k_3, of $^-\alpha\alpha\cdot$ dissociation is not much different from that of the decomposition of $^-DD\cdot$ (about 1 sec^{-1}), we conclude that the association constant of $^-\alpha\alpha\cdot + \pi\cdot^-$ into $^-\alpha\alpha\text{–}\pi^-$ is of the order of $10^3\ M^{-1}\ sec^{-1}$. This is reasonable because the rate constants of some similar reactions, which were determined directly,[17] are of this order.

The oxidation of $^-\alpha\alpha^-$ by benzpyrene[15] proceeds like the oxidation by pyrene. The adduct formation is evident from spectrophotometric studies, and the self-retardation by the resulting benzpyrene radical ions is demonstrated by kinetic investigations.

It is instructive to compare the results obtained in the systems $^-\alpha\alpha^-$ + aromatic for anthracene, pyrene, and benzpyrene. The pertinent data are collected in Table III. The most interesting finding becomes evident when columns 2 and 3 are compared with the 4 and 5. The change in the electron affinity of the acceptor is reflected, virtually quantitatively, in the equilibrium leading to the adduct formation. The relevant equilibrium constants vary by several powers of 10. On the other hand, neither the equilibrium

$$^-\alpha\alpha\text{–aromatic}^- \rightleftharpoons {}^-\alpha\alpha\cdot + \text{aromatic}\cdot^-$$

nor the rates of the forward or backward reactions are much affected by the electron affinity of the hydrocarbon. It seems that the factors which facilitate the rupture of the bond and the formation of the aromatic

Table III

$$^-\alpha\alpha^- + \text{aromatic} \rightleftharpoons {}^-\alpha\alpha\text{–aromatic}^- \qquad K_{add}$$

$$^-\alpha\alpha\text{–aromatic}^- \longrightarrow {}^-\alpha\alpha\cdot + \text{aromatic}\cdot^- \qquad k_{decomp}$$

$$^-\alpha\alpha\cdot + \text{aromatic}\cdot^- \longrightarrow {}^-\alpha\alpha\text{–aromatic}^- \qquad k_{comb}$$

Aromatic	Electron affinity,[a] V	K_{add}, M^{-1}	$k_{decomp} \times 10^2$, sec^{-1}	Rel k_{comb}
Anthracene	0.642	$>10^5$	0.9–1.6	1
Pyrene	0.529	120	1.1–1.5	1.2
Benz[*e*]pyrene	0.484	...	~3	0.4

[a] Relative electron affinity in THF (biphenyl = 0): J. Chaudhuri, J. Jagur-Grodzinski, and M. Szwarc, *J. Phys. Chem.*, **71**, 3063 (1967).

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[17] S. C. Chadha, J. Jagur-Grodzinski, and M. Szwarc, *Trans. Faraday Soc.*, **63**, 2994 (1967).

radical ion favor also the reverse reaction. Aromatic hydrocarbon of greater electron affinity forms a stronger $^{-}\alpha\alpha$–aromatic^{-} bond as well as more stable aromatic$\cdot^{-}$ radical ion.

Conclusions

The electron-transfer processes involved in the oxidation of the dicarbanions, $^{-}\mathrm{DD}^{-}$ and $^{-}\alpha\alpha^{-}$, by aromatic hydrocarbons are initiated by equilibria such as

$$^{-}\mathrm{DD}^{-} + \mathrm{A} \rightleftarrows {}^{-}\mathrm{DD}\cdot + \mathrm{A}\cdot^{-} \text{ or } {}^{-}\alpha\alpha\cdot\mathrm{A}^{-} \rightleftarrows {}^{-}\alpha\alpha\cdot + \mathrm{A}\cdot^{-}$$

These equilibria lie far to the left, because the electron affinity of $^{-}\mathrm{DD}\cdot$ or $^{-}\alpha\alpha\cdot$ radicals are much higher than those of the investigated acceptors. Hence, only a minute concentration of $^{-}\mathrm{DD}\cdot$ or $^{-}\alpha\alpha\cdot$ is maintained in the system, and the decomposition of these radicals, *viz.*

$$^{-}\mathrm{DD}\cdot \longrightarrow \mathrm{D}\cdot^{-} + \mathrm{D} \text{ or } {}^{-}\alpha\alpha\cdot \longrightarrow \alpha\cdot^{-} + \alpha$$

provides a sink which drives the over-all reaction to the right.

The radical $^{-}\mathrm{DD}\cdot$ is formed directly through electron-transfer process arising from a bimolecular collision between $^{-}\mathrm{DD}^{-}$ and the acceptor. On the other hand, the investigated acceptors form an adduct, $^{-}\alpha\alpha$–aromatic^{-} with $^{-}\alpha\alpha^{-}$, which in turn decomposes into $^{-}\alpha\alpha\cdot$. This indirect route is more favorable than a direct electron transfer. The reaction with Pe$\cdot^{-}$ is an exception. In this system $^{-}\alpha\alpha\cdot$ is formed directly in a bimolecular process.

Formation of adducts is not limited to the monoadduct. A diadduct, $^{-}$aromatic-$\alpha\alpha$–aromatic^{-}, is also formed, but the latter contributes only a little to the oxidation. Its formation accounts for the curious observation that the rate of $^{-}\alpha\alpha^{-}$ oxidation increases with the initial concentration of the acceptor, but eventually it reaches a maximum and declines when the acceptor concentration becomes sufficiently high.

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Kinetic Isotope Effect in the Radiation-Induced Decomposition of Crystalline Potassium Nitrate[1]

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Contribution from the Department of Chemical Engineering,
University of Maryland, College Park, Maryland. *Received May 27, 1969*

Abstract: A kinetic isotope effect in the radiolysis of crystalline $\mathrm{KN^{18}O_3}$ has been observed which has a maximum of 19 ± 3% at an absorbed dose of 0.5×10^{21} eV/g. The isotope effect is explained by the simultaneous occurrence of two reaction paths which produce an additive isotope effect. One of these paths involves an exciton-induced reaction of randomly diffusing oxygen molecules at preferred lattice sites. The amount of decomposition occurring *via* this reaction path is a function of the concentration of these "preferred" sites which in the case of most inorganic solids is on the order of 10^{17}–10^{19} per cm^3. The other reaction path is that associated with direct decomposition of excited or ionized nitrate ions.

The radiation-induced decomposition of crystalline potassium nitrate by electrons and γ rays has been the subject of numerous investigations.[2-15] The stoichiometry of the room-temperature decomposition is generally accepted to be

$$\mathrm{KNO_3} \rightsquigarrow \mathrm{KNO_2} + {}^{1}\!/_{2}\mathrm{O_2} \qquad (1)$$

The room-temperature decomposition was shown to exhibit an abnormally high isotopic effect in the oxygen fragment[7] (~13%); however, this effect was only observed in the initial stages of the decomposition (~0.8 mole %). The yield of product as a function of absorbed dose was linear and could be represented as two straight lines intersecting at an absorbed dose of about 7×10^{21} eV/g giving rise to an apparent "break" in the plot, the isotope effect being observed only in the region prior to the "break." A diffusion-controlled mechanism (2), where the oxygen fragment initially produced diffuses away from the $\mathrm{NO_2^-}$ simultaneously formed, was postulated and the isotope effect was explained by the Franck–Rabinowitch cage effect and the jump frequency of the oxygen fragment. The isotope effect was only evident in the oxygen,

$$\mathrm{KNO_3} \rightsquigarrow [\mathrm{KNO_2} + \mathrm{O}] \qquad (2)$$

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(1) Research conducted under the auspices of the U. S. Atomic Energy Commission Contract No. AT(40-1)-3660.

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