Formation of Bimolecular and Termolecular Complexes of Tetrahalo-*p*-benzoquinones with a Variety of Nonaromatic Donors

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Received November 19, 1987

A spectrophotometric investigation has been conducted of the interaction of *p*-chloranil and *p*-fluoranil in carbon tetrachloride (25.0 °C) with a variety of structural types of donors which, with one exception, are not aromatic. The donors used included certain aliphatic iodides, carbonyl compounds, esters, amides, lactones, and lactams. The experimental results have been used initially to evaluate equilibrium constants on the assumption that only 1:1 tetrahalo-*p*-benzoquinone (Ac)–donor (D) complexes are formed. In those cases in which the donors are relatively weak, the experimental data, in fact, provided evidence of the formation of only 1:1 complexes, DAc. Certain of the donors, including some of the carbonyl compounds, the amides, lactams, and some of the lactones, have proved to be sufficiently strong that they form appreciable amounts of termolecular complexes, D_2Ac, as well as 1:1 complexes when the donor concentrations of the media are high. In such cases equilibrium constants for formation of both types of complexes have been evaluated.

Considerable experimental evidence has been presented that π acceptors such as tetracyanoethylene and the tetrahalo-*p*-benzoquinones are functionally capable of coordinating with two as well as with one donor molecule in forming molecular complexes in solutions of aromatic donors.[1-6] It is interesting, however, that the π acceptor 2,7-dinitro-1,6-methano[10]annulene, which is sterically hindered on one side of the annulene ring, forms only 1:1 complexes even when the donor is present in large excess.[7]

In a recent spectrophotometric investigation of the interactions of *p*-chloranil and *p*-fluoranil with a variety of ethers it was observed that certain of the ethers which are relatively strong n donors, as well as some phenolic ethers, also undergo 2:1 as well as 1:1 donor–acceptor complex formation with *p*-fluoranil in carbon tetrachloride solutions of relatively high donor concentrations.[8] Those same ethers on interaction with the strong acceptor iodine monochloride, as well as with iodine, appear to form only 1:1 complexes.[9] Presumably, because of its polar nature, iodine monochloride is functionally incapable of interacting simultaneously with more than one donor molecule.

A detailed UV spectrophotometric study has now been conducted of the interaction of *p*-chloranil and *p*-fluoranil (Ac), in carbon tetrachloride, with a variety of nonaromatic donors (D) of widely differing strengths to elucidate further the conditions under which such donors are disposed to undergo formation of significant amounts of termolecular complexes, D_2Ac. The donors employed in this investigation include various aliphatic iodides, carbonyl compounds, esters, amides, lactones, and lactams. Little information concerning tetrahalo-*p*-benzoquinone complexes of these kinds of donors has been reported previously.

Experimental Section

Materials. Most of the donors were of the best grade available from Aldrich Chemical Co. Butyraldehyde and *N,N*-dimethylformamide, reagent grade and certified ACS grade respectively, were obtained from Fisher Scientific, and 1-iodopropane was obtained from Kodak. The sources of carbon tetrachloride, *p*-chloranil, and *p*-fluoranil (2,3,5,6-tetrahalo-1,4-benzoquinones) are the same as have been reported previously.[8,9]

The Equilibrium Measurements. A series of carbon tetrachloride solutions of the acceptor (ca. 10^{-3} M) and varying concentration of the donor under investigation were prepared at 25.0 °C. The donor concentrations of the solutions were in large excess of the acceptor concentration and varied over a wide range, where feasible of the order of tenfold; the maximum donor concentration attained depended on the molecular weight and solubility of the particular donor used; the minimum concentration was that which provided for sufficient complexing of the acceptor to obtain useful data. For each complex investigated the absorbances (at various ultraviolet wavelengths) of solutions of six or more different donor concentrations were measured. The equipment used and further details of the methods of measurement were the same as described previously.[8,9]

The experimental data obtained at a particular wavelength for the series of solutions of varying donor concentrations were interpreted initially on the assumption that only a 1:1 complex, with an equilibrium constant of K_c, was formed (eq 1). The data were treated graphically by using the Ketelaar eq 2.[10] In eq 1 and 2

$$K_c = [DAc]/[D][Ac] \quad (1)$$

$$\frac{1}{\epsilon_a - \epsilon_{Ac}} = \left(\frac{1}{\epsilon_c - \epsilon_{Ac}}\right)\left(\frac{1}{K_c[D]}\right) + \frac{1}{\epsilon_c - \epsilon_{Ac}} \quad (2)$$

the term Ac represents the acceptor, and in eq 2, $\epsilon_a = A/l[Ac]_t$ where A is the absorbance of the solution in question, l is the light path length in cm, and $[Ac]_t$ is the total acceptor concentration in mol/L (free and complexed), ϵ_{Ac} and ϵ_c are the molar absorptivities of free and complexed acceptor, respectively, and [D] is the molar concentration of the donor. Plots of $1/(\epsilon_a - \epsilon_{Ac})$ values at a particular wavelength vs the corresponding 1/[D] values were prepared. In those cases in which the plots were linear over the entire donor concentration range, K_c values later reported were calculated from the slopes and intercepts. In those cases in which the lines curved downward at higher donor concentrations, reported K_c values were based on the linear portions of the plots again by using the slopes and intercepts, the latter as obtained by extrapolation of the lines to the ordinate axis.

Results and Discussion

The Spectra of the Complexes. Figures 1 and 2 provide some insights concerning the influence on the spectra of *p*-chloranil and *p*-fluoranil when these acceptors form complexes with the various types of donors included

(1) Foster, R.; Dodson, B. *J. Chem. Soc. D* **1951**, 1516.
(2) Dodson, B.; Foster, R.; Bright, A. A. S. *J. Chem. Soc. B.* **1971**, 1283.
(3) Bright, A. A. S.; Chudek,J. A.; Foster, R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1256.
(4) Bailey, R. J.; Chudek, J. A.; Foster, R. *J. Chem. Soc., Perkin Trans. 2* 1976, 1590.
(5) Chudek, J. A.; Foster, R.; Jarrett, F. M. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 2729.
(6) Chudek, J. A.; Foster, R.; Twiselton, D. R. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1385.
(7) Chudek, J. A.; Foster, R.; Vogel, E. *J. Chem. Soc., Perkin Trans. 2* **1977**, 994.
(8) Andrews, L. J.; Keefer, R. M. *J. Org. Chem.* **1988**, *53*, 537.
(9) Andrews, L. J.; Keefer, R. M. *J. Org. Chem.* **1987**, *52*, 2690.
(10) (a) Ketelaar, J. A. A.; van de Stolpe, C.; Gersmann, H. R. *Recl. Trav. Chim. Pays-Bas* **1951**, *70*, 499. (b) Ketelaar, J. A. A.; van de Stolpe, C.; Goudsmit, A.; Dzcubas, W. *Ibid.* **1952**, *71*, 1104.

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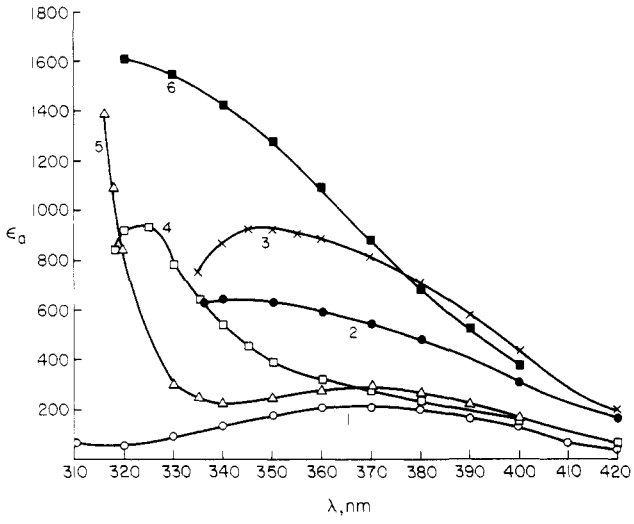


Figure 1. The spectrum of *p*-chloranil in carbon tetrachloride solutions of various donors (25.0 °C). Curve 1, *p*-chloranil in CCl_4; curve 2, in 3.31 M 2,4-pentanedione; curve 3, in 3.97 M 2-iodopropane; curve 4, in 5.21 M 2,5-hexanedione; curve 5, in 4.93 M ϵ-caprolactone; curve 6, in 2.35 M ϵ-caprolactam.

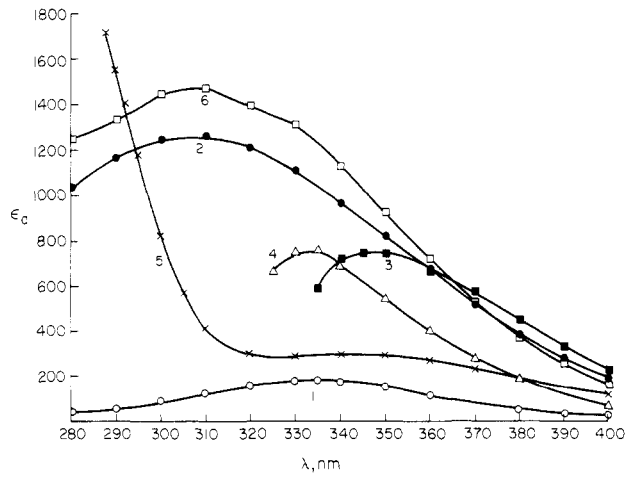


Figure 2. The spectrum of *p*-fluoranil in carbon tetrachloride solutions of various donors (25.0 °C). Curve 1, *p*-fluoranil in CCl_4; curve 2, in 2.21 M *N*,*N*-diethylacetamide; curve 3, in 3.96 M 2-iodopropane; curve 4, in 5.29 M cyclohexanone; curve 5, in 5.10 M ϵ-caprolactone; curve 6, in 2.38 M ϵ-caprolactam.

in this investigation. The degree to which each of the acceptors is bound to the individual donors depends, of course, on the strengths of the various complexes and the donor concentrations of the particular solutions on which the spectrophotometric measurements were made. Figures 1 and 2 illustrate clearly, however, that the complexing of the tetrahalo-*p*-benzoquinones with all of the various types of donors included in this investigation has marked spectral consequences.

Figure 1 focuses on the *p*-chloranil complexes. Curve 3 (2-iodopropane as the donor) is generally representative of the absorption characteristics of all of the iodide donors. Curve 4 for the interaction of 2,5-hexanedione is similar to that for the corresponding interactions of the cyclic ketones, cyclopentanone, and cyclohexanone, and 2,4-pentanedione, though the absorption intensity of the latter complex is considerably lower than that of the other nonaromatic ketone complexes. The acetone complex shows major absorption at significantly lower wavelengths than the other ketone complexes. The butyraldehyde complex spectrum is like that shown in curve 4, except that it has a generally lower absorption intensity. As compared to the cyclopentanone, cyclohexanone, and 2,5-hexanedione complex absorptions, that of the acetophenone–*p*-chloranil complex is shifted toward the visible with a maximum of ca. 350 nm and is of relatively low intensity. It resembles that of the toluene–*p*-chloranil complex but with a lower absorption intensity. This suggests that the primary site of donor activity in acetophenone is the aromatic ring itself rather than the carbonyl group. The complexes of all the lactams and *N*,*N*-dialkyl amides have spectra similar to that shown in curve 6; that of *N*-methylacetamide is shifted to lower wavelengths. Curve 5 is generally representative of all of the complexes of the lactones, and the spectra of vinyl acetate and isopropenyl acetate complexes are similar, though of lower intensity. The spectra of solutions of ethyl acetate and *p*-chloranil in the range of 310–400 nm were closely similar to that of the free acceptor, which precluded equilibrium measurements. Presumably the complex absorption maximum lies below 310 nm, a region in which *p*-chloranil itself absorbs intensely.

The spectra of the *p*-fluoranil complexes with the various types of donors (Figure 2) resemble those of the corresponding *p*-chloranil complexes. In most cases the absorption maxima of the *p*-fluoranil complexes appear at slightly lower wavelengths than those of the corresponding *p*-chloranil adducts.

The Equilibrium Constants

Values of K_c for the various donor–acceptor interactions which were investigated spectrophotometrically were obtained by graphical treatment of the data in terms of the Ketelaar equation (see eq 1 and 2 of the Experimental Section), as has been described in detail previously.[8,9] The plots for the interactions of the relatively weak donors with the tetrahalo-*p*-benzoquinones were linear over a wide range of donor concentrations, extending as high as 5 M or more in some instances. Included in this group of donors which were subject to equilibrium studies were the alkyl iodides, certain of the ketones, butyraldehyde, vinyl and isopropenyl acetates, and δ-butyrolactone.

In those instances in which K_c values for the complexes approached or exceeded 1.0 L mol^{-1} the lines obtained by graphical treatment of the experimental data were straight in the region of low to moderate donor concentration but curved downward at high donor concentration levels. This is considered to reflect the formation of significant amounts of 2:1 complexes (D_2Ac) as well as 1:1 complexes (DAc). Some of the observed curvature may reflect deviations from ideal solution laws though it is doubtful that this is a problem of great significance.[6,7] Figure 3 provides examples of instances in which such deviation from straight lines is observed.

Table I provides a summary of the equilibrium constants for the interactions of the various donors with *p*-chloranil and for a few of the donors with different types of functional groups with *p*-fluoranil in carbon tetrachloride (25.0 °C). Except as noted in the table, in those cases in which the Ketelaar plots of the data were linear throughout the entire donor concentration range, the only equilibrium constants reported are the K_c values as obtained from the slopes and intercepts of the plots.

In those cases in which the Ketelaar plots exhibited noticeable deviations from linearity the method of Deranleau[11] has been applied in estimating K_1 and K_2 (eq 3), as described in detail recently.[8] The K_1 values so obtained

$$K_2 = [D_2Ac]/[D][DAc] \quad (3)$$

(11) Deranleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4044, 4050.

Table I. The K_c, K_1, and K_2 Values for the Tetrahalo-*p*-benzoquinone Complexes (CCl_4 Solvent, 25.0 °C)

donor	[D] range, L mol^{-1}	λ range,[a] nm	K_c,[b] L mol^{-1}	K_1, L mol^{-1}	K_2, L mol^{-1}
		Chloranil Complexes			
iodoethane	3.92–0.490	340–380	0.038 ± 0.003		
1-iodopropane	3.31–0.414	340–380	0.030 ± 0.004		
2-iodopropane	3.97–0.496	350–380	0.075 ± 0.010		
2-iodo-2-methylpropane	3.24–0.810	350–380	0.09 ± 0.02		
1,3-diiodopropane	2.24–0.280	335–360	0.094 ± 0.019		
cyclohexyl iodide	3.09–0.387	335–380	0.16 ± 0.03		
acetophenone	3.31–0.414	370–380	0.30 ± 0.06		
2,4-pentanedione	5.28–0.603	340–370	0.33 ± 0.02		
acetone	8.04–1.01	330–350	0.41 ± 0.04		
n-butyraldehyde	4.60–0.985	332–336	0.48 ± 0.05		
cyclopentanone	6.59–0.581	330–360	0.87 ± 0.11	1.22 ± 0.06	0.17 ± 0.01
cyclohexanone	5.31–0.332	330–350	0.86 ± 0.09	1.13 ± 0.12	0.12 ± 0.01
2,5-hexanedione	5.21–0.163	315–330	1.47 ± 0.07[c]		
vinyl acetate	3.97–0.496	310–320	0.18 ± 0.02		
isopropenyl acetate	4.03–0.504	310–335	0.43 ± 0.03		
N-methylacetamide	5.84–0.365	320–360	0.80 ± 0.08	1.3 ± 0.1	0.19 ± 0.02
N,*N*-dimethylformamide	6.67–0.208	330–360	1.7 ± 0.2	2.4 ± 0.2	0.31 ± 0.01
N,*N*-dimethylacetamide	6.66–0.208	330–390	2.4 ± 0.3	2.9 ± 0.2	0.22 ± 0.02
N,*N*-diethylacetamide	4.55–0.142	330–380	2.4 ± 0.3	3.0 ± 0.3	0.33 ± 0.03
tetramethylurea	3.95–0.124	330–390	2.6 ± 0.2	3.5 ± 0.2	0.34 ± 0.03
γ-butyrolactone	6.68–0.501	310–316	0.34 ± 0.03		
δ-valerolactone	6.07–0.542	320–325	0.50 ± 0.05	0.72 ± 0.04	0.110 ± 0.005
ε-caprolactone	4.93–0.466	314–324	1.08 ± 0.10	1.48 ± 0.10	0.18 ± 0.02
ε-caprolactam	2.35–0.074	320–380	2.6 ± 0.5	4.2 ± 0.6	0.65 ± 0.06
δ-valerolactam	2.41–0.075	320–380	3.5 ± 0.3	5.5 ± 0.2	0.86 ± 0.07
		Fluoranil Complexes			
2-iodopropane	4.44 ± 0.494	345–370	0.081 ± 0.004		
cyclohexanone	5.29 ± 0.331	330–350	1.7 ± 0.2	2.0 ± 0.2	0.17 ± 0.03
N,*N*-diethylacetamide	4.42–0.138	340–380	7.2 ± 0.3	7.9 ± 0.2	0.34 ± 0.02
ε-caprolactone	5.10–0.159	295–305	4.8 ± 0.3	5.8 ± 0.3	0.45 ± 0.02
ε-caprolactam	2.38–0.074	280–380	6.4 ± 0.5	8.3 ± 0.4	1.1 ± 0.1

[a] Reported values of K_c, K_1, and K_2 are averages of values calculated from data collected at several wavelengths in this range. [b] The values of K_c which are <0.1 are not highly reliable since they are based on Ketelaar plot intercepts which are small and not subject to accurate evaluation. [c] At high donor concentrations the Ketelaar plots deviated from linearity; in that region, however, the points obtained by plotting $1/(\epsilon_a - \epsilon_{Ac})$ vs $1/[D]$ scattered sufficiently that they could not be fitted to a curve with sufficient accuracy to permit estimation of K_1 and K_2 values.

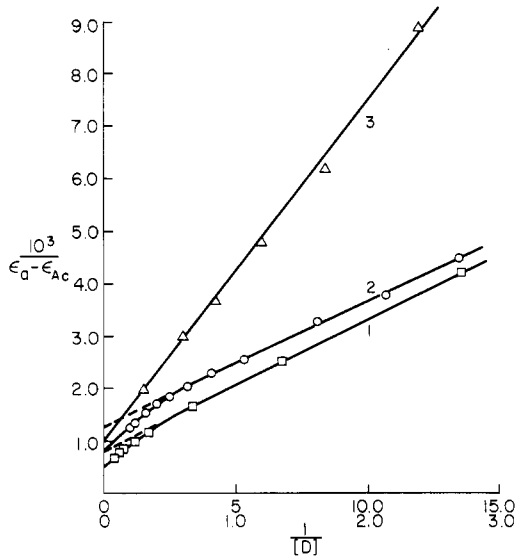


Figure 3. Plots for the determination of the apparent equilibrium constants (K_c) of several chloranil complexes using the Ketelaar equation. Curve 1, 1.13×10^{-3} M chloranil and ε-caprolactam (λ 330 nm) using upper abscissa; curve 2, 1.13×10^{-3} M chloranil and ε-caprolactone (λ 320 nm) using lower abscissa; curve 3, 1.10×10^{-3} M chloranil and 2,4-pentanedione (λ 340 nm) using lower abscissa.

are, in effect, K_c values which have been corrected in recognition of the formation of termolecular as well as bimolecular complexes. A typical example of the results obtained by use of the Deranleau procedure in treating the spectrophotometric data recorded at different wavelengths is provided in Table II.

Table II. Equilibrium Constants and Molar Absorptivities of DAc and D_2Ac Complexes of ε-Caprolactone and *p*-Chloranil (CCl_4, 25.0 °C)

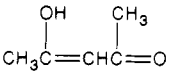
λ,[a] nm	K_1, L mol^{-1}	K_2, L mol^{-1}	K_c, L mol^{-1}	ϵ_1	ϵ_2
324	1.37	0.165	0.93	390	910
322	1.33	0.156	0.96	510	1110
320	1.45	0.169	1.06	630	1380
318	1.58	0.197	1.16	790	1620
316	1.52	0.181	1.16	1080	2090
314	1.62	0.211	1.21	1340	2550

[a] Wavelength of the measurements.

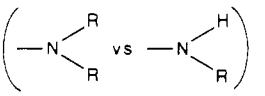
The ϵ_1 and ϵ_2 values listed in the table are the molar absorptivities of the 1:1 and 2:1 complexes, respectively. The K_c, K_1, and K_2 values reported in Table I are the averages of values obtained from data recorded at several wavelengths. The K_1 values are somewhat larger than K_c, and in most instances K_2 values are of the order of one-tenth the K_1 values. It is assumed that in those cases in which Ketelaar plots of the data were linear the K_c values reported are reasonably representative of K_1 values.

The results summarized in Table I show clearly that the iodides are the weakest donors and, as such, exhibit no *observable* tendency to undergo termolecular complex formation. This is not meant to imply that no termolecular complexes are formed in such cases but only that they do not exist in sufficient quantity to be apparent under the experimental methods employed. The open chain alkyl (mono)iodo compounds appear to increase somewhat in donor strength in complexing with *p*-chloranil (cf. K_c

values) in the order primary < secondary < tertiary, probably as a result of varying inductive effects of the alkyl groups. 1,3-Diiodopropane is a noticeably stronger donor than iodoethane and 1-iodopropane, a fact which probably reflects the statistical advantage of two donor sites in the molecule. The cycloalkanones and 2,5-hexanedione are sufficiently strong donors to undergo 2:1 complex formation with *p*-chloranil. This diketone is a substantially better donor than the (mono)carbonyl compounds, again probably in reflection of a statistical factor. Unlike the hexanedione, 2,4-pentanedione is not a very strong donor, one which like acetone and butyraldehyde shows no significant inclination to form a termolecular complex. This no doubt reflects the fact that in nonpolar media 2,4-pentanedione exists largely in the enol form,[12] The ace-



tophenone–*p*-chloranil complex, in which the aromatic ring is the presumed donor site, is slightly weaker than the corresponding toluene complex[8,13] in reflection of the differences in inductive effects of methyl and acetyl groups. As a group the amides and the lactams used in this investigation are all relatively strong donors and demonstrate a disposition to form termolecular complexes. The lactones as donors are weaker than the *N,N*-dialkyl amides and the lactams, and, in fact, γ-butyrolactone is weak enough not to show evidence of 2:1 complex formation. Donor strengths of the lactones in their interactions with *p*-chloranil increase with increasing donor ring size for reasons which are not apparent. This is not the case for the two lactams included in the study. The *p*-chloranil complex of *N*-methylacetamide is weaker than the corresponding *N,N*-dialkyl amide complexes, presumably because of differences in the inductive effects of hydrogen atoms and alkyl groups In complexing with *p*-chloranil



vinyl acetate is a rather weak donor as compared to the lactones. Conjugation of the ester function with a carbon–carbon double bond is probably the underlying factor. Isopropenyl acetate is a better donor, though not a very strong one, possibly because of the favorable inductive effect of the methyl group attached to its carbon–carbon double bond.

With the exception of 2-iodopropane the various kinds of donors which have been investigated form markedly stronger complexes with *p*-fluoranil than with *p*-chloranil, as might be expected. The superiority in acceptor strength of *p*-fluoranil over *p*-chloranil was also apparent in the study of their interactions with ethers.

In summary, it can be concluded that the tendency of the tetrahalo-*p*-benzoquinones, (acceptors which offer two potential coordination sites, one on each face of the planar molecules) to form termolecular complexes is by no means restricted to aromatic π donor systems.[14] It appears to be a rather general phenomenon which is observed with relatively strong donors (those with relatively high K_c values) of varied structural type and in donor–acceptor solutions of relatively high donor concentration.

(12) Cf.: Hine, J. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1962; p 242 and references contained therein.
(13) Fukuzumi, S.; Kochi, J. K. *J. Org. Chem.* **1981**, *46*, 4116.
(14) An example of 2:1 complex formation between *p*-chloranil and a nonaromatic amine has been reported by: Campbell, J. M.; Demetrious, B.; Jones, R. J. *J. Chem. Soc., Perkin Trans. 2* **1983**, 917.

Reactivity of Superoxide Ion with Thioamides in Dimethyl Sulfoxide

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Received April 30, 1987

The first step in the reaction of $O_2^{\bullet-}$ with thioamides (thiobenzamide, thionicotinamide, thioisonicotinamide, 2-ethyl-4-pyridinethiocarboxamide [ethionamide], thioacetamide, and thioacetanilide) in dimethyl sulfoxide is nucleophilic addition. Subsequent reaction of the initially formed peroxythiolate anion with a second $O_2^{\bullet-}$ yields O_2 and the peroxythiolate dianion; the latter undergoes nucleophilic addition with a second thioamide to give, after cleavage, 2RC(S$^-$) = NH + HOOH. The overall stoichiometry is one $O_2^{\bullet-}$ per thioamide. The formed thioamide anion and O_2 slowly react to form the corresponding nitrile (RC≡N), polysulfides, and a second HOOH. The rates of reaction for the primary step have been evaluated via rotated ring-disk voltammetry under pseudo-first-order conditions; the apparent second-order rate constants range from 115 ± 15 M^{-1} s^{-1} for thioacetamide to (6 ± 1) × 10^3 M^{-1} s^{-1} for thioacetanilide in dimethyl sulfoxide at 25 °C.

Previous studies[1-5] have demonstrated that superoxide ion ($O_2^{\bullet-}$) in aprotic media reacts with carbonyl carbons via nucleophilic addition. With esters the alkoxide is a good leaving group and there is net hydrolysis via subsequent reduction of the percarboxylate radical by a second

(1) Sawyer, D. T.; Stamp, J. J.; Menton, K. A. *J. Org. Chem.* **1983**, *48*, 3733.
(2) Johnson, R. A. *Tetrahedron Lett.* **1976**, 331.
(3) San Filippo, J., Jr.; Chern, C.-I.; Valentine, J. S. *J. Org. Chem.* **1976**, *41*, 1077.
(4) San Fillipo, J., Jr.; Romano, L. J.; Chern, C.-I.; Valentine, J. S. *J. Org. Chem.* **1976**, *41*, 586.
(5) Gibian, M. J.; Sawyer, D. T.; Ungermann, T.; Tangpoonpholvivat, R.; Morrison, M. M. *J. Am. Chem. Soc.* **1976**, *101*, 640.

0022-3263/88/1953-2166$01.50/0