J. Am. Chem. Soc. **1983**, *105*, 6845–6849 6845

764-42-1; methyl acrylate, 96-33-3; acrylonitrile, 107-13-1; maleic anhydride, 108-31-6; methanol, 67-56-1; ethanol, 64-17-5; isopropanol, 67-63-0; diphenyl fumarate, 6338-19-8; *trans*-1,3-pentadiene, 2004-70-8; styrene, 100-42-5; *trans,trans*-2,4-hexadiene, 5194-51-4; 2,5-dimethyl-2,4-hexadiene, 764-13-6; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8; trimethylethylene, 513-35-9; cyclohexene, 110-83-8; *trans*-1,2-dichloroethylene, 156-60-5; *cis*-propenylbenzene, 766-90-5; *cis*-1,2-dichloroethylene, 156-59-2; *trans*-propenylbenzene, 873-66-5; acetonitrile, 75-05-8; dimethyl maleic anhydride, 766-39-2; bis[1-(9-fluorenylidenimine)ethylidene], 87319-56-0; 2,2-dimethyl-3-(2-methyl-1-propenyl)spiro[cyclopropane-1,9′-(9*H*)fluorene], 87319-57-1; *cis*-2-methyl-3-phenylspiro[cyclopropane-1,9′-(9*H*)fluorene], 87319-58-2; *trans*-2-methyl-3-phenylspiro[cyclopropane-1,9′-(9*H*)fluorene], 87319-59-3; *trans*-2-methyl-3-ethylspiro[cyclopropane-1,9′-(9*H*)fluorene], 87319-60-6; *cis*-2-methyl-3-ethylspiro[cyclopropane-1,9′-(9*H*)fluorene], 87319-62-8; *cis*-2,3-dichlorospiro[cyclopropane-1,9′-(9*H*)fluorene], 87319-63-9; *trans*-2,3-dichlorospiro[cyclopropane-1,9′-(9*H*)fluorene], 87319-64-0; 9-ethynyl-9-fluorenol, 13461-74-0; cyclohexane, 110-82-7.

Kinetics and Mechanism of the Interaction of Potassium Peroxydisulfate and 18-Crown-6 in Aqueous Media

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Abstract: A kinetic investigation of the interaction of potassium peroxydisulfate with the crown ether 18-crown-6 in basic aqueous media has shown that the crown ether has a tremendous accelerating effect upon the rate of disappearance of peroxydisulfate. This acceleration is due in part to a radical chain mechanism in which crown is oxidized, and which is similar to that observed in the presence of simple ethers. However, an additional crown effect is observed which is explicable in terms of a Coulombic attraction between a cation-complexed crown radical and the peroxydisulfate dianion.

Potassium peroxydisulfate is well known as a free radical initiator in emulsion polymerization reactions[1] and as an oxidant in aqueous media.[2] More general utilization of this relatively inexpensive peroxide has been limited, perhaps, due to the fairly high activation energy (33.5 kcal/mol in basic media[3]) for homolytic scission of the peroxidic linkage. A more serious deterrent to its use is its general insolubility in organic solvents and only modest solubility (5.3 g/100 cm^3 at 20 °C[4]) in aqueous media.

We recently reported[5] that phase transfer catalysts allow utilization of peroxydisulfate as a polymerization initiator in organic media. The surprising efficiency of these "phase transfer free radical polymerizations" led us to speculate[6] that a "naked" peroxydisulfate (**1**) might be expected to exhibit enhanced tendencies toward fragmentation to sulfate radical anions (**2**) because of increased Coulombic repulsion between the anionic termini of "naked" **1**.

$$\underset{\textbf{1}}{{}^{-}OSO_2O{-}OSO_2O^{-}} \longrightarrow \underset{\textbf{2}}{2\ SO_4^{-}}$$

Table I. Influence of Temperature and Additives on Rate of Decomposition of Potassium Peroxydisulfate[a]

temp, °C	additive	*k* (L/mol s)	E_a (kcal/mol)	ln *A*	$\Delta S^{\ddagger}$ (cal/mol deg)
40	18-crown-6[b]	1.65×10^{-2}	19.9	31.9	2.6
45	18-crown-6[b]	2.25×10^{-2}			
50	18-crown-6[b]	4.02×10^{-2}			
55	18-crown-6[b]	6.45×10^{-2}			
60	18-crown-6[b]	1.08×10^{-1}			
50	diglyme[c]	3.78×10^{-3}	29.0	43.8	25.8
60	diglyme[c]	2.18×10^{-2}			
70	diglyme[c]	5.01×10^{-2}			
50	none[d,e]	1.1×10^{-6}	33.5[f]	43.4[g]	25.5[g]
50	none[d]	1.0×10^{-6}[f]			

[a] $[K_2S_2O_8]_0 = 0.01$ M. [b] 0.12 M. [c] 0.24 M. [d] First-order reaction, units of *k* are s^{-1}. [e] This work. [f] Reference 3. [g] Calculated from the data given in ref 3.

Table II. Dependence of Initial Rates on Peroxydisulfate Concentration

$[S_2O_8^{2-}]$ (mol/L)	I.R. (mol/L s)
2.5×10^{-3}	8.0×10^{-7}
4.8×10^{-3}	3.6×10^{-6}
7.1×10^{-3}	7.1×10^{-6}
9.7×10^{-3}	1.3×10^{-5}

In order to assess this question, we decided to investigate the kinetics of the thermal decomposition of aqueous potassium peroxydisulfate in the presence of the crown ether 1,4,7,10,13,16–hexaoxacyclooctadecane (18-crown-6).[7] Peroxydisulfate reaction kinetics have been studied extensively in aqueous media in both the absence[3] and presence[8] of ether additives. Although the concept of "naked" ions is seldom considered in the highly solvating medium, water, the rather limited solubility of potassium peroxydisulfate compared to that of the closely analogous salts potassium sulfate (12 g/100 cm^3 at 25 °C[4]) and ammonium peroxydisulfate (58.5 g/100 cm^3 at 0 °C[4]) suggested to us a possible lack of total ionic dissociation and thus a potential source of a crown effect.

The present report details our kinetic investigations of the dramatic accelerating effect that 18-crown-6 has on the rate of

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(4) "CRC Handbook of Chemistry and Physics"; 51st ed.; CRC Press: Cleveland, 1970–1971; p B-127.

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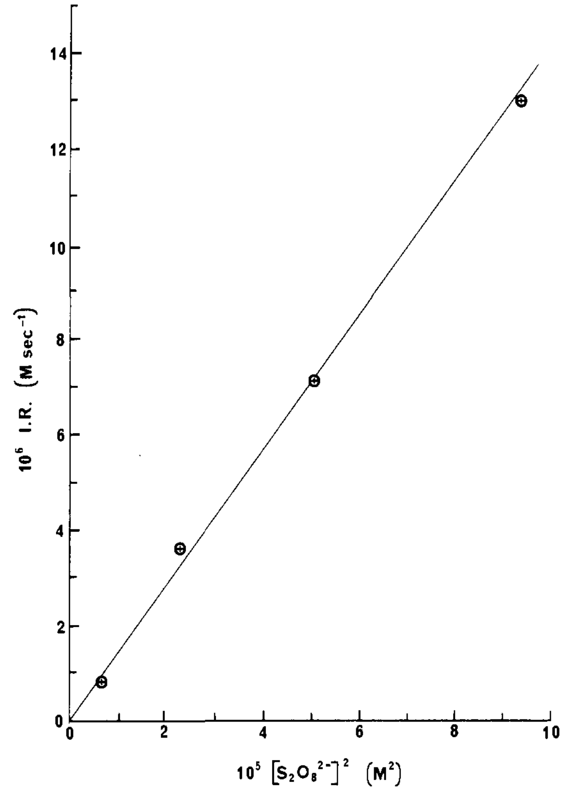

Figure 1. Dependence of initial rate (I.R.) for peroxydisulfate disappearance at 60 °C on the peroxydisulfate concentration squared in the presence of 0.12 M 18-crown-6.

disappearance of potassium peroxydisulfate. This acceleration is due primarily to a radical chain process, in which crown is being oxidized, rather than to the generation of "naked" **1**. In addition, however, an unusual crown effect is implicated as contributing to the acceleration.

Results

Activation Parameters. Since the rate of decomposition of peroxydisulfate is known to be pH dependent and the kinetics are more complicated in acidic media,[3] we decided to investigate the reaction in basic media. The disappearance of potassium peroxydisulfate (initially 0.01 M)[9] in 0.1 M aqueous potassium hydroxide solution was monitored at various temperatures in the presence of 0.12 M 18-crown-6. Throughout the kinetic study we noted what appeared to be an induction period in the reactions containing 18-crown-6. This induction period (about 8 min at 60 °C) was inversely proportional to temperature but displayed little or no relationship to crown ether concentration. After the induction period, decomposition appeared to follow second-order kinetics, and plots of the data were linear to ≥95% disappearance of peroxydisulfate. Rate constants and activation parameters for these and various control reactions are given in Table I.

Rate Law. The kinetic dependence of the reaction on peroxydisulfate concentration was determined at 60 °C with use of a crown concentration of 0.12 M. Initial rates (I.R.) of disappearance of peroxydisulfate are listed in Table II. A plot of –log I.R. vs. –log $[S_2O_8^{2-}]_0$ gave a slope of 2.10, indicating approximate second-order dependence on peroxydisulfate concentration. Figure 1, a linear plot of I.R. vs. $[S_2O_8^{2-}]^2$ that passes through the origin, provides additional evidence for this order.

In Table III are listed the rate data obtained upon varying the crown concentration at an initial peroxydisulfate concentration of 0.01 M. Surprisingly, the rate constant at 60 °C was found to be dependent upon 18-crown-6 only at concentrations less than about 0.025 M, apparently indicating a saturation phenomenon at higher levels of crown. Below this saturation point, as indicated in Figure 2, the order in 18-crown-6 concentration is approximately one-third. Thus, the rate law that most closely fits the experimental data for the concentration ranges studied is

$$-d[S_2O_8^{2-}]/dt = k[S_2O_8^{2-}]^2[\text{18-crown-6}]^{1/3}$$

Table III. Influence of 18-Crown-6 Concentration at 60 °C

[18-crown-6] (mol/L)	k (L/mol s)	I.R. (mol/L s)
5.5×10^{-4}	8.76×10^{-3}	1.7×10^{-6}
5.0×10^{-3}	6.31×10^{-2}	4.1×10^{-6}
1.1×10^{-2}	9.70×10^{-2}	4.7×10^{-6}
2.0×10^{-2}	9.93×10^{-2}	6.6×10^{-6}
5.5×10^{-2}	1.08×10^{-1}	9.5×10^{-6}
1.2×10^{-1}	1.08×10^{-1}	

Table IV. Influence of Additives and Buffer on Rate Constant at 60 °C

buffer	additive (mol/L)	10^2k (L/mol s)
KOH	18-crown-6 (0.02)	9.93
KOH	15-crown-5 (0.02)	7.85
LiOH	18-crown-6 (0.02)	5.85
KOH	18-crown-6 (0.02)/diglyme (0.04)	2.48

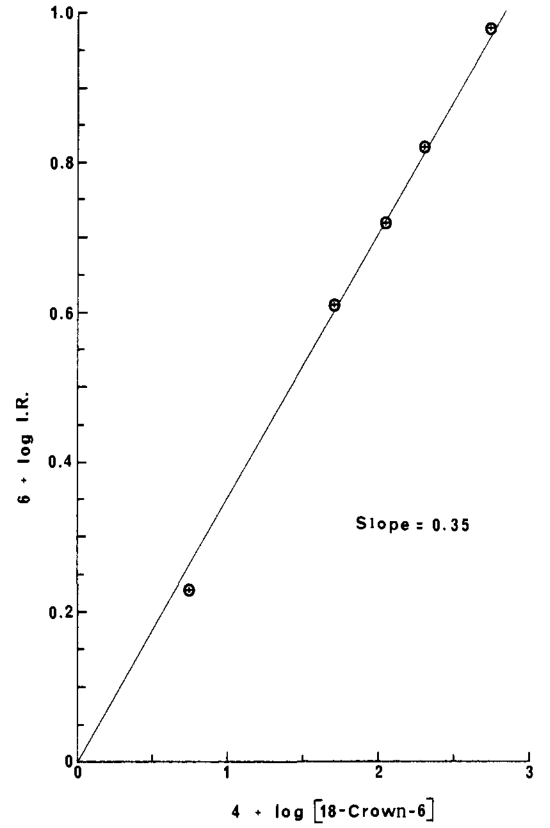

Figure 2. Dependence of –log I.R. for peroxydisulfate disappearance at 60 °C on –log [18-crown-6].

Results obtained upon varying other reaction parameters are listed in Table IV.

UV Spectral Changes. Throughout the kinetic study, concomitant with the beginning of disappearance of peroxydisulfate, we noted the appearance of a yellow coloration in the reaction mixtures that deepened as the reaction proceeded. Due to the apparent correspondence of the color formation to the disappearance of peroxydisulfate, we decided to investigate the reaction spectrophotometrically. A typical reaction mixture was monitored by ultraviolet spectroscopy in the region 400–200 nm. At zero time, the only absorption maximum was at 223 nm, due to the peroxydisulfate. Within 15 min, a new absorption had appeared

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[9] At higher peroxydisulfate concentrations, decomposition was so rapid that exotherms were observed in the reaction mixtures even at 30 °C.

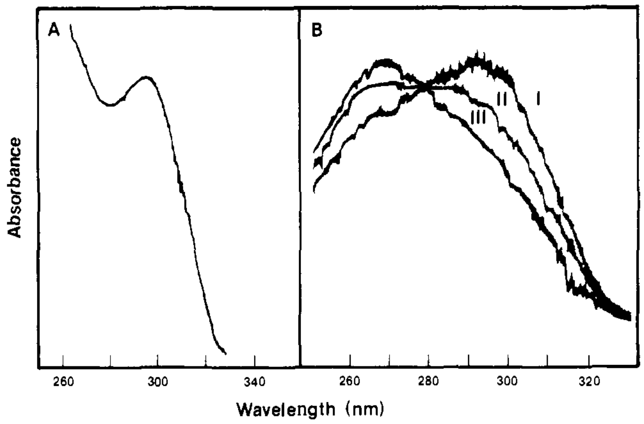


Figure 3. Ultraviolet absorption spectra of reaction mixtures from the interaction of potassium peroxydisulfate (0.01 M) with 18-crown-6 (0.02 M) at 60 °C in 0.1 N KOH solution: (A) reaction time 15 min; (B) reaction mixtures diluted 1 to 10—curve I 60 min, curve II 120 min, curve III 240 min.

at 295 nm (Figure 3A) that continued to grow in intensity over the next 45 min. At a total reaction time of 60 min, a shoulder began to appear at 268 nm. The 268-nm absorption grew at the expense of the 295-nm peak until, at 240 min, only the former remained. An isosbestic point in the absorption spectra (Figure 3B) indicated that the transient was probably a direct precursor of the final 268-nm absorbing species. Reactions conducted in the presence of diethyleneglycol dimethyl ether (diglyme) in lieu of crown ether displayed similar spectral changes although intensities were greatly reduced.

Radical Trapping Agents. Radical scavengers have been used to help elucidate the mechanism of certain peroxydisulfate reactions.[10] The favorite scavenger, allyl acetate, could not be used in our study because of the high pH, while the nucleophilic radical trap quinoxaline[11] itself increased the rate of peroxydisulfate decomposition approximately 50-fold. Decomposition therefore was studied in the presence of 0.02 M methacrylonitrile. At 60 °C the rate of the crown (0.12 M)-mediated reaction was suppressed to approximately the same as that in the presence of methacrylonitrile alone.

Discussion and Conclusions

The results listed in Table I indicated that the addition of 18-crown-6 had a dramatic accelerating effect upon the rate of disappearance of peroxydisulfate. It soon became apparent, however, that this effect was not due to the formation of a "naked" peroxydisulfate ion. No indication of association between potassium ions and peroxydisulfate could be demonstrated from either conductivity or ion selective electrode measurements. In addition, the change in reaction order, and finally the suppression of the accelerating effect in the presence of methacrylonitrile, argued against a simple unimolecular decomposition mechanism.

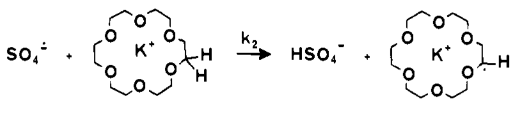
The oxidation of alkyl ethers by peroxydisulfate in neutral aqueous media has been thoroughly studied by Edwards, Gallopo, and co-workers.[8] A free radical chain mechanism was found to be operative under these conditions with the following rate law:

$$-d[S_2O_8^{2-}]/dt = k[S_2O_8^{2-}]^{3/2}$$

The presence of an induction period and the inhibition of the reaction by methacrylonitrile provide strong evidence that a radical chain mechanism is a major contributor to the rate acceleration in the presence of crown ethers as well. However, the dramatic differences between the reaction in the presence of 18-crown-6 and that in the presence of diglyme (Table I) indicate a somewhat more complicated situation. Since both additives have similar kinds of abstractable hydrogen atoms, one is compelled to propose an additional crown effect. The data listed in Table IV indicate that complexation may be an important part of this effect. Substitution of 15-crown-5 for 18-crown-6 led to a 21% reduction in rate, presumably because of the weaker potassium ion complexing ability of 15-crown-5.[12] Similarly, substitution of lithium for potassium hydroxide buffer solution again lowered the rate, this time by 41%, the expected result of poor complexation of Li^+ by 18-crown-6. In further support of this idea, examination of the decomposition of tetrabutylammonium peroxydisulfate in aqueous tetrabutylammonium hydroxide buffer revealed only a minor difference in rates between runs containing added 18-crown-6 or diglyme.

It seems reasonable that the overall reaction mechanism in the presence of crown ethers is similar to that reported[8] for the oxidation of simple ethers by peroxydisulfate. Rate suppression in the presence of methacrylonitrile supports the usual initiation step[10] (eq 1). The propagation steps with crown ether involvement are presumably those depicted by eq 2 and 3.

$$S_2O_8^{2-} \xrightarrow{k_1} 2\ SO_4^{\cdot-} \qquad (1)$$



(2)

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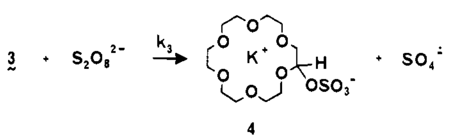

(3)

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The apparent existence of a crown effect might then be explicable in one of two possible ways. The first of these concerns the relative ease of hydrogen abstraction from complexed and noncomplexed polyethers, respectively. Hydrogen abstraction may be strongly facilitated in the complexed state due to either weakened carbon-hydrogen bond strength upon complexation or increased stabilization of the resultant radical via through-space interaction with the cation. Rate acceleration would then be mediated through eq 2. A second possibility that could account for the rate acceleration involves a Coulombic contribution due to the cationic nature of the complexed crown ether species in eq 2 and 3.

Differentiation between the two cases can be easily accomplished by conducting the reaction in the presence of both 18-crown-6 and diglyme. If hydrogen abstraction is responsible for the acceleration (eq 2), abstraction from the complexed crown would have to be faster than that from diglyme in order for a crown effect to be observed, and one would expect no change or perhaps a slightly faster rate of peroxydisulfate disappearance in the presence of both additives. On the other hand, if the rate of hydrogen abstraction is comparable for the two ether substrates, but fast in comparison to the rate-influencing induced decomposition step (eq 3), a rate reduction is anticipated under the proposed reaction conditions. Similarly, consideration of Coulombic contributions leads to the same conclusions regarding the outcome of the control reaction.

The experiment (entry 4, Table IV) resulted in a lower rate constant by a factor of 4, indicating that Coulombic attraction in step 3 must be the origin of the crown effect. Since the addition of diglyme statistically reduces the likelihood of hydrogen abstraction from the crown by a factor of about 2, this must also mean that abstraction from diglyme is faster than that from complexed crown. On the basis of the known geometry of 18-

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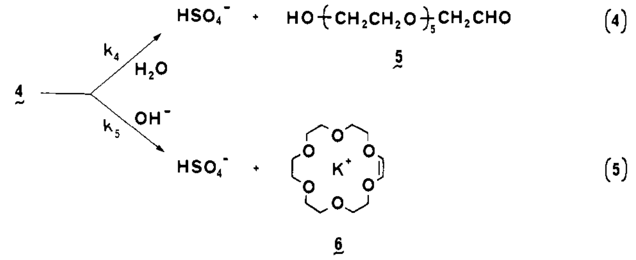
crown-6/potassium ion complexes[13] and recent results[14] on the stereoelectronic effects of hydrogen atom abstraction from ethers, one would not expect a significant difference in rate of abstraction from 18-crown-6 vs. diglyme under our conditions due to a conformational effect. The dihedral angle between the C–H bond and the p-type orbital (with its associated pair of electrons) on the oxygen of both substrates should be nearly 30°. Thus the apparent lower rate of abstraction from crown is probably due to the fact that the p-type orbital is also the one involved in potassium ion complexation and therefore is less available for stabilizing the incipient radical.

Subsequent to steps 2 and 3, several further reactions are possible. Equations 4, 5, and 6 are analogous to reactions proposed[8] for the oxidation of simple ethers and may, in part, be used to explain the UV spectral observations. A likely candidate for the transient species exhibiting 295-nm absorption would be an α-alkoxyaldehyde such as aldehyde **5**. 2-Ethoxybutyraldehyde, for example, exhibits λ_{max} 312 nm in cyclohexane solvent.[15] Under the basic conditions of our study, however, the reaction depicted by eq 4 appears less likely than that of eq 5 as the pathway for breakdown of sulfate **4**. It does not seem reasonable for oxidized crown **6** to absorb at 295 nm since crown ether **8** exhibits a λ_{max} of only 300 nm (CH_2Cl_2).[16] Therefore we propose β scission (eq 7) as an alternative process leading to alkoxyaldehydes. The formation of the yellow color in the reaction as well as of the final 268-nm-absorbing product is probably due to aldol products derived from either **5** or **7** or other similar crown decomposition products. That aldehyde-containing products are formed in the reaction was indicated by spectroscopic examination of material recovered by extraction of the aqueous reaction mixture with toluene. Along with a major amount of crown ether, the extract contained a component (~13%) that exhibited characteristic aldehyde absorptions in the infrared and ^1H NMR spectra.



$$2\ \underset{\sim}{3} \xrightarrow{k_6} \text{Products} \qquad (6)$$

$$\underset{\sim}{3} \xrightarrow{k_7} \cdot CH_2CH_2\{OCH_2CH_2\}_4OCH_2CHO \qquad (7)$$

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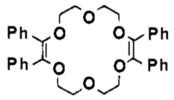

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Some additional comments need be made concerning the substantial differences between our experimentally derived rate law and the rate law reported by Edwards[8] for the oxidation of simple ethers. First of all, the difference in terms of peroxydisulfate order may be explained by the fact that our study was conducted in a highly alkaline medium (pH ~13). Sulfate radical anion **2** is known to undergo quite rapid reaction with hydroxide ion (eq 8), displaying a rate constant only slightly lower than that

$$SO_4^{-\cdot} + HO^- \longrightarrow HO^\cdot + SO_4^{2-} \qquad (8)$$

for reaction of **2** with methacrylonitrile.[17] If one assumes that eq 8 is competitive with eq 2, it is not unreasonable that the order in peroxydisulfate concentration would be increased relative to the $^3/_2$ value found in neutral media.[18] Second, the fact that we have observed a dependence upon crown concentration whereas Edwards' results were independent of ether concentration may be due simply to the fact that the latter study was conducted in the presence of at least a 10-fold excess of ether vs. peroxydisulfate. In this respect, the partial order dependency on crown concentration may be attributed to multiple oxidation of the crown ether (or species derived from it). Unsaturated crown ether **6** or aldehydes such as **5** or **7** would be expected to be nearly as reactive toward radical species, if not more so, than would 18-crown-6 itself. Thus, competition is to be expected at low crown concentrations.

Finally, the enhancement of a reaction rate due to *increased* interaction between a crown-complexed cation and the corresponding anion deserves particular mention. This, in general, is opposed to the commonly observed increases in anion reactivity effected by complexation and *removal* of the counterion.[19] It is interesting to note that catalysis of reactions of anionic nucleophiles by cationic centers near the reaction site may be explained at least in part by electrostatic interactions (enthalpic factors).[20,21] The results of Rastetter,[21] for example, provide evidence that a crown–potassium ion complex may function catalytically as a template for macrolide ring closure, although definitive rate data have not as yet been reported. More recently, kinetic evidence has been presented[22] on the necessity of cation binding in the facilitation of an electron-transfer-initiated reduction reaction involving potassium tri-*sec*-butylborohydride. The present study represents, to our knowledge, the first example of catalysis of a radical oxidation reaction by a crown–cation complex. Examples of complex formation and associated electrostatic catalyses such as these appear to be simple models for many enzyme-mediated reactions, and further studies along these lines will be potentially rewarding.[22]

Experimental Section

All experiments were conducted by utilizing distilled-deionized water. Potassium peroxydisulfate (Mallinckrodt Analytical Reagent) was recrystallized from distilled-deionized water and dried under vacuum prior to use. 18-Crown-6, 15-crown-5, methacrylonitrile, and diethyleneglycol dimethyl ether were utilized as supplied by Aldrich Chemical Co. Lithium hydroxide (Fisher) was used as obtained commercially. Standard potassium hydroxide solutions were prepared by using DILU-T-IT (J. T. Baker Analytical concentrate). Glassware was washed throughly, then rinsed three times with distilled-deionized water and oven dried overnight prior to use.

Peroxydisulfate Analyses. Peroxydisulfate was determined by an indirect Coulometric measurement, using ferrous ion as the intermediate reagent. A solution of 0.1 M $FeSO_4$/0.5 M H_2SO_4 was placed in a Coulometric cell and electrolyzed (platinum working and counterelectrodes) at 0 V vs. saturated calomel to zero current (actual background was less than 5 μA with a nitrogen flow maintained over the electrode surface). A 0.1-mL portion of the reaction mixture was added with an Eppendorf pipet, and the resulting cathodic current was integrated with a PAR Model 379 Digital Coulometer. The same cell solution could be used for the sequential analysis of 20 or more 0.1-mL samples. Per-

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[18] Alternatively, a referee has pointed out that the true order may indeed be $^3/_2$ and that some aldehyde inhibition intrudes, a possibility which we have not addressed experimentally.

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[22] Wagner, W. R.; Rastetter, W. H. *J. Org. Chem.* **1983**, *48*, 294-298.

oxydisulfate concentration was calculated by using the following equation:

$$[S_2O_8^{2-}] = \frac{(\text{coulombs})}{96.5(0.1)(2)}$$

Typical Procedure. The following example is typical of the general procedure used in the kinetic runs. Two stock solutions were freshly prepared: stock solution A, 0.02 M $K_2S_2O_8$ in 0.2 M KOH; stock solution B, 0.24 M 18-crown-6. A 50-mL aliquot of stock solution A was placed in a 250-mL round-bottomed 2-necked flask fitted with a thermometer and equilibrated in a constant temperature bath to 60 ± 0.1 °C. After equilibration to 60 °C a 50-mL aliquot of stock solution B was transferred to the flask, giving final concentrations of 0.12 M 18-crown-6 and 0.01 M $K_2S_2O_8$ in 0.1 M KOH. The flask was shaken to ensure good mixing, and a sample (about 0.5 mL) was withdrawn to mark zero time. Samples were then withdrawn periodically for analyses until 90-95% disappearance of peroxydisulfate. Upon withdrawal, each sample was quenched by rapid cooling to 0 °C. Successive analyses showed no change in peroxydisulfate concentration at 0 °C over several hours.

UV Study. A typical run (0.01 M $K_2S_2O_8$, 0.02 M 18-crown-6 in 0.1 M KOH, 60 °C) was repeated. Samples were examined by recording spectra utilizing a Cary Model 14 spectrophotometer in the region 400-200 nm vs. a blank solution identical with the reaction mixture except that the peroxydisulfate was omitted.

Product Study. The reaction mixture following a kinetic run was continuously extracted with toluene for 2 days. The yellow residue obtained upon evaporation of the solvent displayed spectral properties very similar to those of 18-crown-6 with the following exceptions: IR (neat) 1700 cm^{-1} (weak absorption); NMR τ (Me_4Si, $CDCl_3$) −0.10 (s); comparison of the intensity of this aldehyde proton absorption to the intensity of the ^{13}C satellite peak of the crown ether methylenes allowed estimation of 13% aldehyde in the mixture.

Registry No. Potassium peroxydisulfate, 7727-21-1; 18-crown-6, 17455-13-9.

Thermolysis of Acyclic Azoalkanes: Simultaneous or Stepwise C-N Homolysis?

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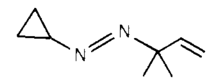
Abstract: Irradiation of several *trans*-α,α-dimethylallylazoalkanes produces the thermally labile cis isomers. Among their thermolysis products, we have found "turnaround" azoalkanes (TA) corresponding to recombination of alkyldiazenyl radicals (RN=N·) at the primary end of the dimethylallyl radical. The amount of TA decreases when R· is a better radical, suggesting a competition between β scission of RN=N· and recombination to give starting azoalkane and TA. A stepwise, internal-return mechanism correctly predicts when formation of TA will be important.

The mechanism by which azoalkanes lose nitrogen has been debated since Ramsperger[1] first posed the question in 1929 right up to the present day. Two mechanisms have received the most attention: simultaneous cleavage of both C-N bonds (A) and stepwise homolysis via a diazenyl radical (B). When the

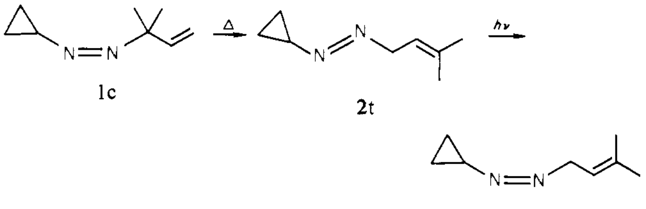
$$R_1N{=}NR_2 \rightarrow R_1\cdot\ N{\equiv}N\ \cdot R_2 \qquad (A)$$

$$R_1N{=}NR_2 \rightarrow R_1N{=}N\cdot\ \cdot R_2 \rightarrow R_1\cdot\ N{\equiv}N\ \cdot R_2 \qquad (B)$$

azoalkane is symmetrical, most of the previous evidence has favored (A),[2] but highly unsymmetrical azoalkanes (e.g., R_1 = Ph, R_2 = α,α-dimethylallyl) clearly decompose via mechanism (B).[3] Our assessment of the situation in 1980 was "azoalkane thermolysis seems to proceed by a continuum of mechanisms between (A) and (B); the more unsymmetrical the azo compound, the more unsymmetrically it cleaves".[4,5] A recent MNDO calculation on azoethane[6] and a solution-phase pressure study of azo-1-adamantane[7] have led to the conclusion that even symmetrical azoalkanes may decompose by stepwise homolysis. Presently, we report evidence for mechanism B with the first step reversible[8] for thermolysis of cis and trans acyclic azoalkanes.



1t



1c

2t

2c

Irradiation of **1t**[9,10] in C_6D_6 at 25 °C with a nitrogen laser (337 nm) produced two new azoalkanes (**2t** and **2c**) along with the usual mixture of hydrocarbons (cf. Figure 1). Although independent irradiation of **2t** gave **2c**, the fact that both isomers built up at equal rates from **1t** shows that these "turnaround" azoalkanes (TA) arise from **1t**. The intermediacy of **1c** was shown by UV

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(1) Ramsperger, H. C. *J. Am. Chem. Soc.* **1929**, *51*, 2134.

(2) For the exception, see: Crawford, R. J.; Takagi, K. *J. Am. Chem. Soc.* **1972**, *94*, 7406. These results are consistent with the mechanism advocated here since internal return is absent in the gas phase. The thermolysis rate should therefore depend only on the strength of the weaker C-N bond.

(3) Porter, N. A.; Dubay, G. R.; Green, J. G. *J. Am. Chem. Soc.* **1978**, *100*, 920.

(4) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

(5) On the basis of an elegant series of experiments, Seltzer expressed the same viewpoint 8 years earlier. Tsolis, A.; Mylonakis, S. G.; Nieh, M. T.; Seltzer, S. *J. Am. Chem. Soc.* **1972**, *94*, 829. See also: Hinz, J.; Oberlinner, A.; Ruchardt, C. *Tetrahedron Lett.* **1973**, 1975.

(6) Dannenberg, J. J.; Rocklin, D. *J. Org. Chem.* **1982**, *47*, 4529.

(7) Neuman, R. C.; Binegar, G. A. *J. Am. Chem. Soc.* **1983**, *105*, 134.

(8) Reversible cleavage for phenylazotriphenylmethanes was first proposed by Pryor, See: Pryor, W. A.; Smith, K. *J. Am. Chem. Soc.* **1967**, *89*, 1741.

(9) Azocyclopropane was recently reported. Engel, P. S.; Gerth, D. B. *J. Am. Chem. Soc.* **1981**, *103*, 7689.

(10) Prepared by the method of: Baldwin, J. E.; Brown, J. E.; Hofle, E. *J. Am. Chem. Soc.* **1971**, *93*, 788.

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