for all values of i from 1 to n (where n is conveniently 1000) the corresponding concentrations of S$^•$ and A$^•$ ([S$^•$] being iterated to any required degree of precision, 0.001% in our calculations) and summing the appropriate expressions for the rates of formation of the various products. Depending slightly on the relative values of the rate constants, each calculation takes a few seconds on a Digital VAX 6210.

Registry No. **1a**, 93754-90-6; **1b** (R = H), 54821-21-5; **1c**, 98395-36-9; **2a**, 4428-13-1; **4b**, 121862-05-3; Ad$^•$, 2819-03-6; D_2, 7782-39-0; Ph_2CO, 119-61-9.

Mechanism of the Thermal Decomposition of Substituted Tetraoxanes in Benzene Solution: Effect of Substituents on the Activation Parameters of the Unimolecular Reactions

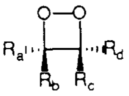
L. F. R. Cafferata,* G. N. Eyler, E. L. Svartman, A. I. Cañizo, and E. J. Borkowski

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Sucursal 4, Casilla de Correo 16, (1900) La Plata, Argentina

Received April 4, 1989

The kinetics and mechanism of the thermal decomposition reactions of three substituted tetraoxanes (benzophenone diperoxide, cyclohexanone diperoxide, and pinacolone diperoxide in benzene solution were investigated in the temperature range 108–165 °C. The activation parameters for unimolecular reactions of molecules of this type are interpreted in terms of substituent effects in the tetraoxacyclohexane ring. Isokinetic relationships are established which characterize a valid "reaction series" for the unimolecular thermolysis reactions of the substances considered, except for the acetone diperoxide homolysis. A general reaction mechanism for the thermolysis of the diperoxides is presented.

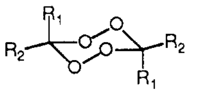
The thermolysis of dioxetanes of the general formula I where R_a, R_b, R_c, and R_d are aliphatic, alicyclic, polycyclic, or aromatic substituents have been the subject of intense mechanistic studies.[1] For example, it has been found that



I

the substitution in a series of 3,3-disubstituted 1,2-dioxetanes yields a systematic increase of less than 1 kcal mol^{-1} per alkyl group in the activation energies of their unimolecular decomposition reactions[2,3] and the replacement of a methyl by a phenyl group makes no change whatever in the respective activation parameters.[4] However, the introduction of 3,4-cyclic substituents produces larger effects on the thermolysis activation parameters.[5]

For some substituted tetraoxanes (ACDP–APDP–BKDP) the experimental evidence indicates thermal decomposition initiated by the formation of biradicals and not through concerted processes.[6-8] However, the ther-



ACDP: $R_1 = R_2 = CH_3$
APDP: $R_1 = CH_3$; $R_2 = C_6H_5$
BKDP: $R_1 = R_2 = C_6H_5CH_2$
BPDP: $R_1 = R_2 = C_6H_5$
CHDP: $R_1–R_2 = –(CH_2)_5–$
PDP: $R_1 = CH_3$; $R_2 = t\text{-}C_4H_9$

molyses are complicated in certain cases (ACDP and BKDP) by induced decomposition reactions. It must be noted that the diperoxides APDP and PDP, with different R_1 and R_2 substituents, can exist in either cis and trans configurations, but in the former case the trans isomer is more stable.[9]

Table I. Rate Constant Values for the Thermolyses of Substituted Tetraoxanes in Benzene Solution

diperoxide	temp, °C	$10^3 m$, mol kg^{-1}	$10^5 k_{exp}$, s^{-1}	$10^5 k_o$,[a] s^{-1}
BPDP	130.7	17.2	0.26	0.26
	140.2	8.37	0.63	0.63
	150.3	9.54	1.61	
		18.6	1.63	1.62
	160.0	9.48	6.55	6.55
	165.5	6.23	8.54	8.54
CHDP	108.0	55	0.17	0.17
	120.5	40	0.76	0.76
	135.0	41	2.30	2.30
	150.0	55	22.0	22.0
	160.0	23	33.4	
		41	39.5	
		55	35.7	
		121	34.2	35.7 ± 2.3
PDP	120.0	15.2	3.57	
		92.4	3.40	3.49 ± 0.09
	140.0	7.1	25.1	
		15.2	28.8	
		170	28.3	27.4 ± 1.6
	160.0	7.1	135	
		170	125	130 ± 5

[a] Errors as standard deviations.

In this work we report the kinetics and mechanism of the thermal decomposition reactions in benzene solution of three substituted tetraoxanes (BPDP, CHDP, PDP) for comparison of their activation parameters with those corresponding to the unimolecular homolyses of the diperoxides ACDP, APDP, and BKDP.[6-8]

Results and Discussion

The thermal decomposition reactions of BPDP, CHDP, and PDP in benzene solution in the temperature and initial

---

(1) Baumstark, A. L.; Retter, Ch. A.; Tehrani, K.; Kellogg, C. *J. Org. Chem.* **1987**, *52*, 3308.

(2) Baumstark, A. L.; Niroomand, F.; Vâsquez, P. C. *J. Org. Chem.* **1984**, *49*, 4497.

(3) O'Neal, E.; Richardson, W. H. *J. Am. Chem. Soc.* **1970**, *92*, 6553.

(4) Richardson, W. H.; Montgomery, F. C.; Yelvington, M. B.; O'Neal, H. E. *J. Am. Chem. Soc.* **1974**, *96*, 7525.

(5) Baumstark, A. L.; Wilson, C. E. *Tetrahedron Lett.* **1981**, *22*, 4363.

(6) (a) Cafferata, L. F. R.; Eyler, G. N.; Mirifico, M. V. *J. Org. Chem.* **1984**, *49*, 2107. (b) Cafferata, L. F. R.; Eyler, G. N.; Mirifico, M. V. *Ibid.* **1985**, *50*, 3245.

(7) Cafferata, L. F. R.; Mirifico, M. V. *An. Asoc. Quim. Argent.* **1986**, *64*, 501.

(8) Cafferata, L. F. R.; Svartman, E. L. *An. Asoc. Quim. Argent.* **1988**, *76*, 261.

(9) Blandon, P.; McCullough, K. J.; Morgan, A. R.; Nonhebel, D. C.; Pauson, P. L.; White, G. J. *J. Chem. Res. Synop.* **1980**, *9*, 284.

0022-3263/90/1955-1058$02.50/0

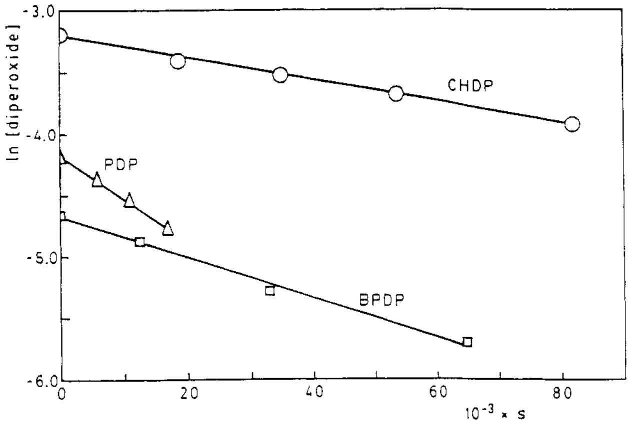


Figure 1. Representation through first-order kinetic plots of the data obtained in typical pyrolysis experiments of the diperoxides (□, BPDP, 150.3 °C; ○, CHDP, 120.0 °C; and △, PDP, 120.0 °C).

concentration ranges shown in Table I follow first-order kinetic laws up to ca. 50% diperoxide conversions (Figure 1). Under these conditions, the corresponding rate constants for CHDP and PDP (k_{exp}, Table I) are practically independent of the initial diperoxide concentrations in approximately 6-fold and 24-fold ranges, respectively, and the mean values can be assigned to the unimolecular reactions (k_0, Table I). These results reflect the lack of induced decomposition reactions of the diperoxides, at least under the experimental conditions investigated, because if such were the case, the rates of the thermolyses would be increased. This behavior is similar to that seen in the APDP thermolysis,[7] but differs from that seen with ACDP and BKDP diperoxides.[6,8] These decomposition processes, which in the case of these molecules are initiated by methyl and benzyl free radicals, respectively, yield oxygen, acetone, and methyl isopropyl ether for ACDP and benzyl phenyl acetate for BKDP. In the initial concentration ranges investigated in this work for BPDP, the nature of the pertinent reaction products (Table II) indicates the lack of induced decomposition reactions in its thermolysis mechanism, validating the assertion that the rate constant actually correspond to the unimolecular homolysis. As a point of fact, at higher temperatures and initial diperoxide concentrations induced decomposition processes cannot be ruled out. The temperature effect on the k_0 values can be represented by the following equations where the errors shown are standard deviations of least mean square data treatments.

$$\ln k_{\mathrm{BPDP}}\ (\mathrm{s}^{-1}) = (33.0 \pm 4.0) - (36900 \pm 1100)/RT$$

$$\ln k_{\mathrm{CHDP}}\ (\mathrm{s}^{-1}) = (32.4 \pm 3.0) - (34600 \pm 1000)/RT$$

$$\ln k_{\mathrm{PDP}}\ (\mathrm{s}^{-1}) = (29.0 \pm 3.0) - (30600 \pm 600)/RT$$

The linearity of these Arrhenius equations over relatively large temperature ranges (Table III) suggests that the calculated activation parameter values for the BPDP, CHDP, and PDP reactions belong to a single process, which could be their respective unimolecular homolyses.

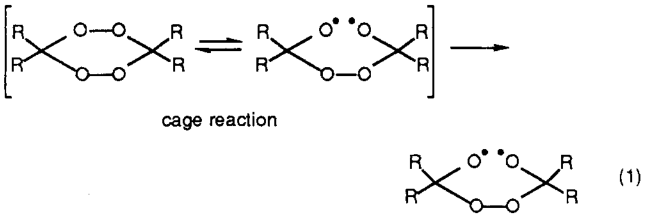
Furthermore, the activation parameters (Table III) lie within the range corresponding to the unimolecular thermolyses in solution of several dialkyl and diacyl peroxides, as well as to other cyclic diperoxides.[6-8] It is expected that the postulated concerted processes[10,11] for these types of molecules would have significantly lower $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values than those obtained in the present work. The alternative possibility of concerted reactions can also be rejected in the cases of CHDP and PDP molecules, on the basis of the comparatively very small yields of cyclohexanone and pinacolone reaction products, respectively, actually observed (Table II). The high yield of benzophenone can be rationalized by considering the relatively low thermodynamic stability of the phenyl free radicals (see below eq 2a and 2b).

Table II. Product Molar Yields in the Thermolyses of Diperoxides (Moles of Product per Mole of Diperoxide Decomposed) in Benzene Solution (ca. 30% Conversion) at 140 °C

diperoxide	$10^3 m$,[a] mol kg^{-1}	$R_1C(O)R_2$	R_1R_2	other products
BPDP	5.7	1.92	0.1	phenol (0.1)
	14.1	1.84	0.1	phenol (0.1)
CHDP	41.0	0.01	-	cyclodecane (0.5) 11-undecanelactone (0.4)
PDP	126	0.19	ethane[b]	toluene (0.4), methyl acetate (0.2), methane,[b] neopentane[b]

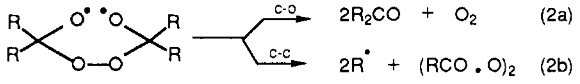
[a] Initial diperoxide concentrations. [b] Qualitative determination.

Thus, the thermolysis mechanism of the diperoxides in solution is initiated by a process of the following type (eq 1) where the rate of ring cyclization within the reaction cage should be a relatively fast step.



(1)

The thermal decomposition reactions of the diperoxides investigated in this work (BPDP–CHDP–PDP) yield products (Table II) which can best be accommodated by the general mechanism shown in eq 2–7.



$$\longrightarrow 2R_2CO + O_2 \quad (2a)$$

$$\longrightarrow 2R^{\bullet} + (RCO\,.\,O)_2 \quad (2b)$$

$$(RCO\,.\,O)_2 \longrightarrow 2RCO\,.\,O^{\bullet} \longrightarrow 2R^{\bullet} + CO_2 \quad (3)$$

$$R^{\bullet} + PhH \longrightarrow (PhHR)^{\bullet} \xrightarrow[-RH]{R^{\bullet}} PhR \quad (4)$$

$$Ph^{\bullet}(R^{\bullet}) + O_2 \longrightarrow Ph(R)O_2^{\bullet} \xrightarrow[-R^{\bullet}]{RH} Ph(R)O_2H \longrightarrow PhO^{\bullet}(RO^{\bullet}) + HO^{\bullet} \quad (5)$$

$$PhO^{\bullet}(RO^{\bullet}) \xrightarrow[-R^{\bullet}]{RH} PhOH(ROH) \quad (6)$$

$$Ph^{\bullet}(R^{\bullet}) + HO^{\bullet} \longrightarrow PhOH(ROH) \quad (7)$$

A primitive view of the thermolyses of all the diperoxides considered in this work suggests that, since biradicals are initially formed (eq 1), the kinetics of the corresponding unimolecular reactions would not be subject to significant substituent effects. In principle, those differences observed in the activation parameters of the unimolecular thermolyses which lie well outside experimental error (Table III) may correspond to inductive, electrostatic, and/or steric effects due to the substituents on the peroxidic bond rupture of the tetraoxane ring, and/or on the biradical-like

---

(10) McCullough, K. J.; Morgan, A. R.; Nonhebel, D. C.; Pauson, P. L. *J. Chem. Res. Synop.* **1980**, *2*, 36.

(11) Richardson, W. H.; Anderegg, J. H.; Price, M. E.; Tappen, W. A.; O'Neal, H. E. *J. Org. Chem.* **1978**, *43*, 2236.

Table III. Activation Parameters and Rate Constants for the Unimolecular Thermolyses of Substituted Tetraoxanes in Benzene Solution

substituted tetraoxane	Δt,[a] °C	n[b]	$\Delta H^{\ddagger}$,[c] kcal mol^{-1}	$\Delta S^{\ddagger}$,[c] cal mol^{-1} K^{-1}	$10^6 k_{140°}$, s^{-1}	ref
ACDP	30	5 (0.997)	35.5 ± 1.1	1.4 ± 0.3	1.1	6
APDP	30	4 (0.999)	39.9 ± 1.0	12.7 ± 1.2	1.5	7
BKDP	40	4 (0.999)	29.8 ± 0.5	−2.7 ± 1.2	158	8
BPDP	33	5 (0.994)	36.1 ± 1.1	6.4 ± 2.0	6.5	this work
CHDP	52	5 (0.993)	33.8 ± 1.0	5.2 ± 1.5	58.7	this work
PDP	40	3 (0.999)	29.8 ± 0.6	−1.5 ± 1.5	256	this work

[a] Experimental temperature range. [b] Number of data points in the Arrhenius equation plot with the corresponding correlation parameters. [c] Values at 140 °C from a least mean square data treatment; errors calculated as in ref 16.

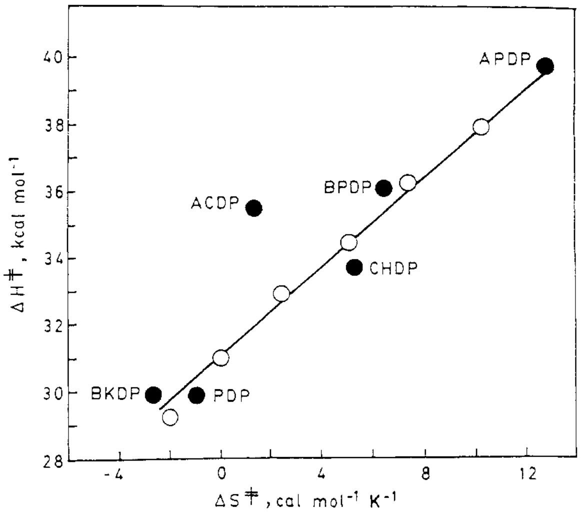


Figure 2. "Isokinetic relationship" according to Leffler and corresponding to the unimolecular thermolyses of several diperoxides in benzene solution, ●; mapped back from the representation ln $k(T_1)$ vs ln $k(T_2)$ of Figure 3, ○.

"transition state" of these reactions.

In the series of the APDP, BPDP, and BKDP molecules the corresponding activation parameters decrease as the steric requirements of the substituents appear to increase, as well. Thus, no compensation effects are observed in the thermolyses of these diperoxide molecules, where the unimolecular reaction rate constant values, at 140 °C, are in the relationship of 1:4:105, respectively. On the other hand, the highly similar activation parameters for the BKDP and PDP molecules, where steric hindrance may be predominant, actually correspond to values which are relatively quite low. To be consistent with this trend, the unimolecular thermolysis of the ACDP diperoxide should be accompanied by activation parameters higher than those actually observed.

The introduction of 3,3- and 6,6-pentamethylene substituents on the tetraoxane ring to form the CHDP molecule does not have a significant effect on the activation parameters of the diperoxide thermolysis, as was observed in the case of the dioxetanes.[2]

A linear relationship between the activation enthalpies and entropies of the unimolecular thermolysis reactions of the diperoxides can be found (Figure 2, r = 0.927; r = 0.990, if the ACDP activation parameters are excluded). It should be noted that the "isokinetic temperature"[12] ($\beta \simeq 406$ °C) is far from the experimental temperatures (108–165 °C), and the ranges of the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values ($\Delta\Delta H^{\ddagger} \simeq 10$ kcal mol^{-1}, $\Delta\Delta S^{\ddagger} \simeq 15$ cal mol^{-1} K^{-1}) are large compared to the probable errors of those parameters. This isokinetic relationship is consistent with the proposed Exner's correlation[13] between the natural logarithms of the rate constants for the same reactions at two different temperatures (Figure 3). In fact, the straight line obtained by plotting ln $k(T_2)$ against ln $k(T_1)$ can be mapped back into the representation $\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$, and vice versa (Figures 2 and 3).

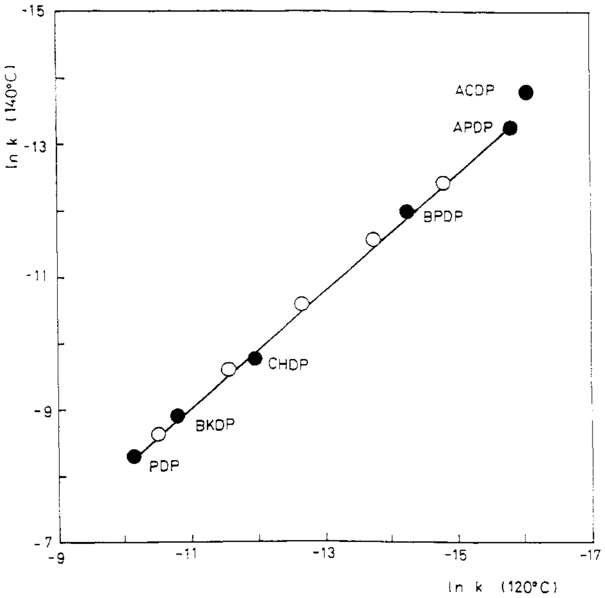


Figure 3. "Isokinetic relationship" according to Exner corresponding to the unimolecular decomposition of several diperoxides in benzene solution, ●; mapped back from the representation $\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$ of Figure 2, ○.

Both graphical treatments support the postulation that some of the reactions considered herein comprise a genuine "reaction series"[14] with a common mechanism, where the substituent effects on the tetraoxacyclohexane ring of the diperoxides affect the values of the kinetic parameters corresponding to the peroxidic bond rupture in benzene solution. Displaced from the straight lines (Figures 2 and 3) is the point corresponding to the ACDP unimolecular reaction, where a different interaction mechanism may be operative. This means that the diperoxides which determine the straight line follow a decomposition mechanism initiated by a unimolecular reaction with similar steric effects in their transition states. The ACDP molecule probably experiences relatively little steric hindrance and very likely, a qualitatively different ground or transition state for its unimolecular reaction. Furthermore, when the isokinetic relationship really holds, in its most general representation ln k vs $1/T$ (Figure 4) must be linear according to the Arrhenius equation, all of the lines must intersect at the point known as the reciprocal isokinetic temperature (β^{-1}). The corresponding isokinetic temperature determined by a statistical method[15] (Figure 4) is 426

---

(12) Leffler, J. E. *J. Org. Chem.* **1955**, *20*, 1202.

(13) Exner, O. *Nature* **1964**, *201*, 488.

(14) Bunnett, J. F. Investigation of rates and mechanism of reaction. In *Techniques of Chemistry*; Weissberger, A., Ed.; Wiley: New York, 1974; Part I, Vol. VI, Chapter VIII.

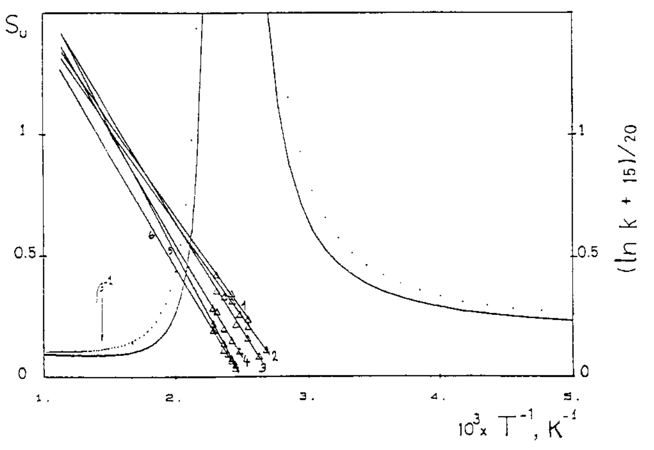


Figure 4. Dependence of the residual sum of squares S_u on the supposed isokinetic temperature T^{-1}. Broken line for all the diperoxides studied; full line for ACDP data excluded. Symbols for the Arrhenius plot are: **1**, PDP; **2**, BKDP; **3**, CHDP; **4**, BPDP; **5**, APDP; and **6**, ACDP.

°C, which is in reasonable agreement with the above β value.

Conclusions

1. The analysis of the reaction products of the thermolyses of some substituted tetraoxanes in benzene solution and the corresponding activation parameters for these unimolecular reactions support a general homolytic stepwise mechanism, rather than a concerted process.

2. A genuine "isokinetic relationship" is observed for the unimolecular homolyses of the acetophenone, benzyl ketone, benzophenone, cyclohexanone and pinacolone diperoxides, which is consistent with similar steric effects in the corresponding transition states of their reactions. The acetone diperoxide reaction deviates from this correlation.

Experimental Section

Materials. The BPDP, CHDP, and PDP diperoxides were prepared by methods described elsewhere,[17] and their purity was checked by GC and IR analysis (KBr, Nujol). Other organic compounds and the benzene solvent were commercial analytical reagents purified by standard techniques.

Kinetic Methods and Product Analyses. Pyrex glass ampoules (7 cm long × 0.8 cm o.d.) half-filled with the appropriate diperoxide solutions thoroughly degassed under vacuum were immersed in a thermostatic silicone oil bath (±0.1 °C) and withdrawn after predetermined times, stopping the reaction by cooling at 0 °C. The diperoxides (except BPDP) remaining in the reaction solutions and their decomposition products were identified by qualitative and quantitative GC analysis (internal standard method, *n*-octane) using a methylsilicone capillary column HP-SP-2100 (12 m × 0.2 mm i.d.) installed in a 5840 A Model Hewlett-Packard instrument (FID), with nitrogen as the carrier gas. Due to the nonvolatile character of the BPDP diperoxide, its quantitative determination in the benzene solutions was performed by a specially designed IR analytical method monitoring the 990 cm^{-1} absorption band. The first-order rate constant values were calculated by a least mean square treatment of the reactions data, and the activation parameters were determined from the corresponding Arrhenius equations.

Acknowledgment. This research project was financially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires. A.I.C. thanks the CIC for a Research Fellowship.

Registry No. BPDP, 16204-36-7; CHDP, 183-84-6; PDP, 124244-55-9.

---

(15) (a) Exner, O. *Nature* **1970**, *227*, 366. (b) Exner, O. *Collect. Czech. Chem. Commun.* **1972**, *37*, 1425.

(16) Huyberechts, S.; Halleux, A.; Kruys, P. *Bull. Soc. Chim. Belg.* **1955**, *64*, 203.

(17) McCullough, K. J.; Morgan, A. R.; Nonhebel, D. C.; Pauson, P. L.; White, C. J. *J. Chem. Res. Synop.* **1980**, 2, 34.

Photoinduced Electron Transfer from Dialkyl Nitroxides to Halogenated Solvents[1]

J. Chateauneuf,[2a] J. Lusztyk,[2b] and K. U. Ingold*,[2b]

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6, and Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

Received June 19, 1989

Laser flash photolysis (LFP) at wavelengths within the charge-transfer absorption present in CCl_4 solutions of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) yields the oxoammonium chloride of TEMPO, 1 (λ_{max} = 460 nm), and the trichloromethyl radical in an essentially instantaneous (≤18 ps) process. The primary photochemical event is an electron transfer from TEMPO to CCl_4, and this is followed by immediate decomposition of the $CCl_4^{\bullet -}$ radical anion to Cl^- and $Cl_3C^\bullet$. An independent synthesis of 1 confirmed that the absorption attributed to this species had been correctly assigned. The formation of $Cl_3C^\bullet$ was inferred by its trapping by molecular oxygen. LFP of TEMPO in other halogenated solvents and of other nitroxides in halogenated solvents has confirmed the generality of these photoreactions.

The photochemistry of *transient* free radicals is a new and rapidly developing subject.[3] It has been found[3] that the high energy content of photoexcited radicals generally does not lead to large increases in the rates of hydrogen atom abstraction,[4] but that these species do have greatly enhanced electron-transfer capabilities. We reasoned that the time-resolved photochemistry of a *persistent* radical should be much easier to study than that of a transient radical. However, a search of the literature revealed that although photolysis of the largest class of persistent rad-

---

(1) Issued as NRCC No. 30777.

(2) (a) Radiation Laboratory. (b) NRC.

(3) Scaiano, J. C.; Johnston, L. J.; McGimpsey, W. G.; Weir, D. *Acc. Chem. Res.*, **1988**, *21*, 22-29.

(4) Excited nitroxides appear to be an exception to this rule.[3,5-8]

0022-3263/90/1955-1061$02.50/0 Published 1990 by the American Chemical Society