pounds. This would then be the most likely possibility for the observation of a dipolar species. Since it is not conclusively observed in this case, no substituent of those commonly investigated would be expected to produce dipolar species.

Experimental Section

The acids were synthesized from the parent anilines using the procedure outlined by Pettit and Irving.[6] Neutralization equivalents were determined for all of the acids and found to agree with the theoretical value within 1%. The neutralization equivalent of the *p*-methoxy compound was that for a monohydrate. Microanalysis for this compound confirmed the result. Microanalyses were carried out by Galbraith Laboratories.

Anal. Calcd for *N*,*N*-di(carboxymethyl)aniline ($C_{10}H_{11}NO_4$): C, 57.41; H, 5.30; N, 6.70. Found: C, 57.49; H, 5.17; N, 6.57.

Anal. Calcd for *N*,*N*-di(carboxymethyl)-4-chloroaniline ($C_{10}H_{10}NO_4Cl$): C, 49.29; H, 4.14; N, 5.75. Found: C, 49.48; H, 4.08; N, 5.60.

Anal. Calcd for *N*,*N*-di(carboxymethyl)-4-fluoroaniline ($C_{10}H_{10}NO_4F$): C, 52.86; H, 4.44; N, 6.17. Found: C, 52.74; H, 4.25; N, 5.99.

Anal. Calcd for *N*,*N*-di(carboxymethyl)-4-methylaniline ($C_{11}H_{13}NO_4$): C, 59.18; H, 5.87; N, 6.28. Found: C, 59.96; H, 6.09; N, 6.21.

Anal. Calcd for *N*,*N*-di(carboxymethyl)-4-methoxyaniline ($C_{11}H_{13}NO_5 \cdot H_2O$): C, 51.36; H, 5.88; N, 5.45. Found: C, 51.51; H, 6.04; N, 5.44.

Nmr spectra of all of the acids were run in NaOD solutions on a Varian A-60. All of the compounds gave the expected aromatic chemical shifts around 6.72–6.92 relative to 3-(trimethylsilyl)-propanesulfonate. The methylene chemical shifts fell between 3.82 and 3.89. The methyl chemical shift in the *p*-methyl compound was 2.22. The methyl shift in the *p*-methoxy compound was at 3.70. Integrated results confirmed the molecular formulas.

The ultraviolet spectra were run on a Beckman DK-2 at 25°. A stock solution of the acid was prepared in dilute sodium hydroxide solution and then added to the final buffer solution. Buffers were chosen which did not absorb in the wavelength region of interest. The reference cell contained buffer. pH measurements were made on a Beckman Research pH meter. Buffer pH's were in steps of one between 1.00 and 10.00. In order to obtain the best set of extinction coefficients an iterative procedure was used. Based on the pH value and the p*K*'s of the acids the concentration of each species was measured. With these values, extinction coefficients were chosen which best fit the absorption change with pH.

The p*K* values for H_2A and HA^- were determined from buffer solutions of these acids at 25° and an ionic strength of 0.100 using KCl as the added electrolyte. A glass electrode–calomel electrode system was used to determine the pH of the solution. The pH meter was calibrated against an acetate buffer and 0.01 *M* HCl. The hydrogen ion concentrations of these buffer solutions are known and the pH reading for the unknown solutions was converted to hydrogen ion concentration. Thus the p*K* values are concentration constants. In some cases the pH of the solution drifted. This was attributed to an acid-catalyzed decarboxylation of the acids. All pH readings were measured as a function of time and extrapolated back to time of mixing. The correction was negligible for the chloro and fluoro compounds and was greatest for the methoxy. However, the pH drift was small and easily measured.

The p*K* of H_3A^+ was determined spectrophotometrically. The acidity of the solutions were adjusted with HCl and the ionic strength was kept constant at the value of 3.0 with KCl. Decomposition proceeded more rapidly at these acidities and all spectra were measured as a function of time. This constant is also a concentration constant.

Acknowledgments.—The authors wish to acknowledge support from the National Science Foundation under Research Grant GP-9034.

---

(6) L. D. Pettit and H. M. N. J. Irving, *J. Chem. Soc.*, 5336 (1964).

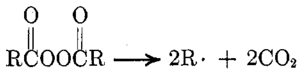
The Reaction of Ionic Thiocyanates with Diacyl Peroxides. The Formation of Thiocyanogen

C. L. JENKINS and J. K. KOCHI*

Department of Chemistry, Indiana University, Bloomington, Indiana 47401

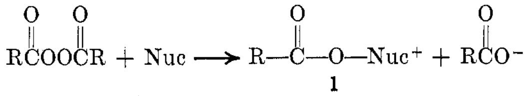
Received March 15, 1971

The thermolysis[1] and photolysis[2] of acyl peroxides represent convenient modes for the production of alkyl radicals, *e.g.*



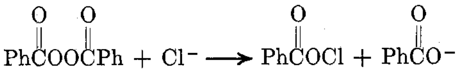
$$\mathrm{R\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}R \longrightarrow 2R\cdot + 2CO_2} \qquad (1)$$

However, complications due to ionic processes can arise by rearrangement to carboxylic carbonic anhydrides involving carboxy inversion.[3] Acyl peroxides are also susceptible to a variety of nucleophiles (Nuc)[4] and the acyloxy intermediate **1** has been shown in a number of



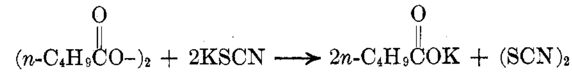
$$\mathrm{R\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}R + Nuc \longrightarrow \underset{\textbf{1}}{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}Nuc^+} + R\overset{\overset{O}{\|}}{C}O^-} \qquad (2)$$

cases to be involved further in competing heterolytic and homolytic processes.[5] Thus, benzoyl hypochlorite, an intermediate in the reaction of benzoyl peroxide and ionic chloride, is capable of electrophilic and free-radical chlorinations.[6]



$$\mathrm{Ph\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}Ph + Cl^- \longrightarrow Ph\overset{\overset{O}{\|}}{C}OCl + Ph\overset{\overset{O}{\|}}{C}O^-} \qquad (3)$$

We wish to report a similar facile reaction when diacyl peroxides are exposed to ionic thiocyanates. Thus, a solution of 0.040 *M* valeryl peroxide and 0.080 *M* potassium thiocyanate in acetonitrile afforded thiocyanogen and potassium valerate according to eq 4 after 5 hr at



$$\mathrm{(\textit{n}\text{-}C_4H_9\overset{\overset{O}{\|}}{C}O\text{-})_2 + 2KSCN \longrightarrow 2\textit{n}\text{-}C_4H_9\overset{\overset{O}{\|}}{C}OK + (SCN)_2} \qquad (4)$$

room temperature. Less than 3% carbon dioxide and no butyl thiocyanate were detected.[7]

---

(1) See A. G. Davies, "Organic Peroxides," Butterworths, London, 1961; E. Hawkins, "Organic Peroxides, Their Formation and Reactions," E. and F. Spon, London, 1961; C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957; W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

(2) R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 4395 (1970).

(3) (a) F. D. Greene, H. S. Stein, C. C. Chu, and F. M. Vane, *ibid.*, **86**, 2081 (1964); (b) C. Walling, H. N. Moulden, J. H. Waters, and R. C. Neuman, *ibid.*, **87**, 518 (1965); (c) H. Hart and D. Wyman, *ibid.*, **81**, 4891 (1959); (d) J. K. Kochi, *ibid.*, **85**, 1958 (1963); (e) R. C. Lamb and J. R. Sanderson, *ibid.*, **91**, 5034 (1969); (f) S. Oae, T. Kashiwagi, and S. Kozuka, *Chem. Ind.* (*London*), 1964 (1965); (g) D. B. Denney and N. Sherman, *J. Org. Chem.*, **30**, 3760 (1965); (h) D. S. Tarbell, *Accounts Chem. Res.*, **2**, 296 (1969).

(4) J. O. Edwards, "Peroxide Reaction Mechanisms," Interscience, New York, N. Y., 1962, p 67 ff.

(5) (a) F. D. Greene, W. Adam, and J. E. Cantrill, *J. Amer. Chem. Soc.*, **83**, 3461 (1961); F. G. Greene and W. Adam, *J. Org. Chem.*, **28**, 3550 (1963); **29**, 136 (1964); (b) Y. Ogata and I. Tabushi, *Bull. Chem. Soc. Jap.*, **31**, 962 (1958); (c) L. Horner and E. Schwenk, *Angew. Chem.*, **61**, 411 (1949); L. Horner and B. Anders, *Chem. Ber.*, **95**, 2470 (1962); C. Walling and N. Indictor, *J. Amer. Chem. Soc.*, **80**, 5814 (1958); C. Walling and R. B. Hodgson, *ibid.*, **80**, 228 (1958); C. Sato and T. Otsu, *Chem. Ind.* (*London*), 125 (1970).

(6) (a) J. K. Kochi, B. M. Graybill, and M. Kurz, *J. Amer. Chem. Soc.*, **86**, 5257 (1964); (b) N. J. Bunce and D. D. Tanner, *ibid.*, **91**, 6096 (1969).

(7) C. L. Jenkins and J. K. Kochi, *J. Org. Chem.*, in press.

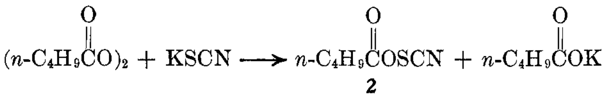
The kinetics of reaction 4 was monitored by following the disappearance of the carbonyl absorption at 1780 cm^{-1} after careful calibration of the system. The reaction between valeryl peroxide and potassium thiocyanate followed clean second-order kinetics (first order in each component) to beyond 80% reaction. The second-order rate constants listed in Table I were invariant with changes in the concentration of each reactant. From the temperature dependence of these second-order rate constants the activation parameters were determined at 25° as $\Delta G^{\ddagger} = 20.6$ kcal/mol, $\Delta H^{\ddagger} = 15.6$ kcal/mol, and $\Delta S^{\ddagger} = -16.8$ eu.

TABLE I

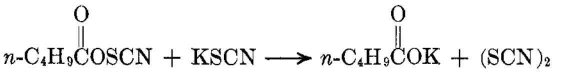
REACTION OF VALERYL PEROXIDE WITH POTASSIUM THIOCYANATE

$(BuCO_2)_2$, $M \times 10$	KSCN, $M \times 10$	Temp, °K	k, M^{-1} sec^{-1}
2.00	4.00	273	1.36×10^{-4}
2.00	0.80	298	1.95×10^{-3}
2.00	2.00	298	1.92×10^{-3}
2.00	1.20	306	3.86×10^{-3}

We deduce from these results that the reaction is a multistep process, and the following mechanism is formulated in which the first step (eq 5) is rate-determining.



$$(n\text{-}C_4H_9\overset{O}{\overset{\|}{C}}O)_2 + KSCN \longrightarrow \underset{2}{n\text{-}C_4H_9\overset{O}{\overset{\|}{C}}OSCN} + n\text{-}C_4H_9\overset{O}{\overset{\|}{C}}OK \qquad (5)$$



$$n\text{-}C_4H_9\overset{O}{\overset{\|}{C}}OSCN + KSCN \longrightarrow n\text{-}C_4H_9\overset{O}{\overset{\|}{C}}OK + (SCN)_2 \qquad (6)$$

Nucleophilic attack by thiocyanate on valeryl peroxide represented by eq 5 compares with the oxidation in aqueous solution of thiocyanate by hydrogen peroxide in which the rate-limiting step was represented[8] as

$$HOOH + SCN^- \longrightarrow \underset{3}{HOSCN} + HO^- \qquad (7)$$

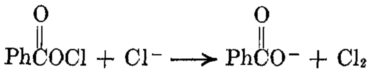
The activation parameters for reaction 7 at 25° are $\Delta H^{\ddagger} = 14.9$ kcal/mol and $\Delta S^{\ddagger} = -25$ eu. These values are similar to those obtained for reaction 5 above, and both sets of activation parameters lie in the range $\Delta H^{\ddagger} = 12$–16 kcal/mol and $\Delta S^{\ddagger} = -15$ to -30 eu, observed for a variety of other nucleophilic displacements on peroxidic oxygen.[9]

Despite the similarity in (a) the kinetics, (b) the rate-determining steps, and (c) the intermediates, the stoichiometries of the reactions between thiocyanate ion and hydrogen peroxide or valeryl peroxide are markedly different. Thus, thiocyanogen was the exclusive product of the oxidation of thiocyanate by valeryl peroxide (eq 4), whereas none was detected when hydrogen peroxide was the oxidant. The stoichiometry of the latter oxidation was represented by the rather complex eq 8.[8]

$$4H_2O_2 + SCN^- \longrightarrow HSO_4^- + HOCN + 3H_2O \qquad (8a)$$

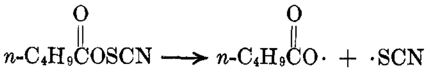
$$HOCN + 2H_2O \longrightarrow NH_4^+ + HCO_3^- \qquad (8b)$$

Following the rate-limiting formation of HOSCN, the postulation of several simultaneous and consecutive reactions involving facile oxidation of the intermediate 3 by hydrogen peroxide was necessitated. The formation of thiocyanogen from the metastable n-$C_4H_9CO_2$-SCN is most readily accommodated by nucleophilic attack on 2 by thiocyanate ion (eq 6). This lability of the oxygen–sulfur bond is analogous to the situation in acyl hypochlorites, in which molecular chlorine is readily formed (eq 9) in the presence of ionic chloride under similar conditions.[6]

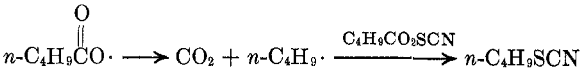


$$Ph\overset{O}{\overset{\|}{C}}OCl + Cl^- \longrightarrow Ph\overset{O}{\overset{\|}{C}}O^- + Cl_2 \qquad (9)$$

The analogy with acyl hypochlorite is somewhat limited, since the Hunsdiecker product[10] derived by homolysis (eq 10) was not represented. The unimportance of such a pathway could be due either to the slow homolysis (eq 10) or the facility of reaction 6 relative to decomposition.[11]



$$n\text{-}C_4H_9\overset{O}{\overset{\|}{C}}OSCN \longrightarrow n\text{-}C_4H_9\overset{O}{\overset{\|}{C}}O\cdot + \cdot SCN \qquad (10)$$



$$n\text{-}C_4H_9\overset{O}{\overset{\|}{C}}O\cdot \longrightarrow CO_2 + n\text{-}C_4H_9\cdot \xrightarrow{C_4H_9CO_2SCN} n\text{-}C_4H_9SCN \qquad (11)$$

In the present study, the reaction of diacyl peroxide with thiocyanate ion has been studied in an inert medium to determine the reactivity and fate of the intermediate 2 in the absence of other reagents. However, this intermediate, RCO_2SCN, represents a potentially active agent for thiocyanation,[12] and reactions with other nucleophiles such as alkenes and arenes would be of interest.

Experimental Section

Materials.—Valeryl peroxide was prepared as described previously.[13] Potassium thiocyanate, n-butyl thiocyanate, and n-butyl isothiocyanate (Eastman Organics) were commercial samples. Acetonitrile was redistilled from phosphorus pentoxide before use.

A solution of thiocyanogen in 75 ml of acetonitrile was prepared by treating 0.0187 mol of bromine in 50 ml of acetonitrile with 0.0218 mol of lead thiocyanate in 25 ml of acetonitrile. The unreacted $Pb(NCS)_2$ and $PbBr_2$ were removed by filtration and the concentration of thiocyanogen was determined by iodometric titration[14] to be 0.246 M.

Analysis.—Valeryl peroxide showed a doublet absorption at 1780 and 1800 cm^{-1} in the infrared region characteristic of diacyl peroxides. The absorbances of the bands were carefully measured in acetonitrile and calibration curves were constructed over the range of relevant concentrations. Valeryl peroxide was also assayed by iodometric titration using ferric chloride (0.02% solution) as a catalyst.[15]

Carbon dioxide was measured by quantitative gas chromatography using the internal standard method with ethane as the marker.[13] Sodium valerate was neutralized and determined quantitatively by gas chromatography on a FFAP column. Thiocyanogen was measured by gas chromatography and iodometric titration.

Kinetics.—Standard solutions of valeryl peroxide and potassium thiocyanate in acetonitrile were mixed in the appropriate ratios

---

[8] I. R. Wilson and G. M. Harris, *J. Amer. Chem. Soc.*, **82**, 4515 (1960); **83**, 286 (1961).

[9] R. Curci and J. O. Edwards, "Organic Peroxides," Vol. I, D. Swern, Ed., Interscience, New York, N. Y., p 199 ff (1970).

[10] *Cf.* F. R. Jensen, L. H. Gale, and J. E. Rodgers, *J. Amer. Chem. Soc.*, **90**, 5793 (1968); C. V. Wilson, *Org. Reactions*, **9**, 332 (1957); R. G. Johnson and R. K. Ingham, *Chem. Rev.*, **56**, 219 (1956).

[11] See J. K. Kochi and R. V. Subramanian, *J. Amer. Chem. Soc.*, **87**, 1508 (1965).

[12] Compare with the electrophilic chlorination using benzoyl hypochlorite reported in ref 6a.

[13] J. K. Kochi, *J. Amer. Chem. Soc.*, **85**, 1950 (1963).

[14] A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed., Wiley, New York, N. Y., p 343 ff.

[15] L. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

to obtain several concentrations of reactants. The reactions were carried out in standard volumetric flasks which were placed in a constant-temperature bath. Samples were removed periodically and analyzed for the extent of reaction. The kinetic runs were carried out under conditions in which the relative concentrations of valeryl peroxide and potassium thiocyanate were varied. Second-order kinetics were followed in each case to beyond 80% reaction.

Registry No.—Thiocyanogen, 505-14-6; valeryl peroxide, 925-19-9; potassium thiocyanate, 333-20-0.

Acknowledgment.—We wish to thank the National Science Foundation and the NDEA for financial support.

tert-Alkylnitroso Compounds. Synthesis and Dimerization Equilibria

JOHN C. STOWELL

Department of Chemistry,
Louisiana State University in New Orleans,
Lakefront, New Orleans, Louisiana 70122

Received February 9, 1971

Kahr and Berther[1] showed that sodium tungstate catalyzed hydrogen peroxide oxidation of primary amines containing an α hydrogen gives oximes. With an amine containing no α hydrogen, this oxidation should give the nitroso compound. In this way we have prepared 2-methyl-2-nitrosopropane in 24% yield.[2] This simple one-step preparation from the inexpensive *tert*-butylamine is more convenient than the previous routes such as $KMnO_4$ oxidation of *tert*-butylamine to the nitro compound[3] followed by Zn–HCl reduction to the hydroxylamine[4] and finally bromine oxidation.[5] The nitroso compound has also been prepared on a small scale by oxidation of *tert*-butylamine vapor with solid *m*-chloroperbenzoic acid.[6] The other product of the H_2O_2 oxidation is 2-methyl-2-nitropropane. Using more H_2O_2 the yield of this nitro compound is 70%. This is a rapid and convenient alternative to permanganate oxidation.

$$RNH_2 + H_2O_2 \xrightarrow{Na_2WO_4} RNO \longrightarrow RNO_2$$

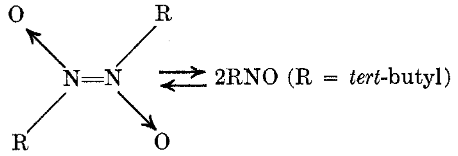
R = *tert*-butyl or 1,1,3,3-tetramethylbutyl

The method functions as well with water-insoluble amines such as 1,1,3,3-tetramethylbutylamine which gives the nitroso compound in 36% yield.

Unhindered aromatic nitroso compounds are monomeric in solution while aliphatic nitroso compounds are dimeric in solution.[7,8] For example, nitrosobenzene is 100% dissociated at 20° in benzene (0.1 *M*) while nitrosocyclohexane is only 0.088% dissociated.[8] The title compounds are exceptions to this. The high steric hindrance of a *tert*-alkyl group favors the monomeric form. For example, we have found that solutions of 2,4,4-trimethyl-2-nitrosopentane in CCl_4 (0.5 *M*) are >99% dissociated by nmr analysis. The equilibrium constants for the *tert*-butyl compound were measured at several temperatures; these and the thermodynamic values are given in Table I.

TABLE I

EQUILIBRIUM CONSTANTS AND THERMODYNAMIC VALUES



K_c = [monomer]^2/[dimer]

Temp, °C (±0.5°)	K_c	ΔG°, cal
35.0	4.85	−968
26.5	2.77	−609
20.0	1.92	−381
9.0	1.06	−33
4.0	0.57	309
0.5	0.43	458

$\Delta H°$ = 11.8 ± 0.3 kcal/mol
$\Delta S°$ = 41.5 ± 1.0 cal/(deg mol)

The $\Delta H°$ is 9 kcal/mol smaller than that for nitrosocyclohexane (20.6 kcal/mol),[8] probably due to the steric bulk of the *tert*-butyl group causing a large amount of crowding in the dimer. This is the opposite of the effect of steric hindrance on aromatic compounds. Ortho substitution favors dimerization; for example, nitrosomesitylene is about 69% dimer. This was explained[9] as steric hindrance to resonance in the monomer which destabilizes the monomer with respect to dimerization.

The per cent dissociation was measured by nmr integration. The spectra of the dimers were obtained by rapid scanning of solutions freshly prepared from the crystalline dimers. These solutions were pale blue but after a few minutes they were deep blue and the spectra showed mostly monomer.

2,4,4-Trimethyl-2-nitrosopentane is thermally unstable. Heating a sample at 150° for 10 min causes complete decomposition giving a variety of products including diisobutylenes and the nitro compound.

Experimental Section

2-Methyl-2-nitrosopropane.—A solution of *tert*-butylamine (36.6 g, 0.50 mol) and $Na_2WO_4 \cdot 2H_2O$ (4.0 g) in 50 ml of water was cooled in an ice bath. Hydrogen peroxide (170 g of 21%, 1.0 mol) was added dropwise over 1.3 hr at 15–20° with stirring.[10]

---

[1] K. Kahr and C. Berther, *Chem. Ber.*, **93**, 132 (1960).

[2] 2-Methyl-2-nitrosopropane is frequently used as a trap for free radicals where the resulting nitroxyl radical can be examined by esr: M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc. B*, 395 (1970); P. Tordo, M. P. Bertrand, and J.-M. Surzur, *Tetrahedron Lett.*, 3399 (1970).

[3] N. Kornblum, R. J. Clutter, and W. J. Jones, *J. Amer. Chem. Soc.*, **78**, 4003 (1956); N. Kornblum, *Org. Reactions*, **12**, 133 (1962).

[4] F. D. Greene and J. F. Pazos, *J. Org. Chem.*, **34**, 2269 (1969).

[5] W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 6522 (1957).

[6] R. J. Holman and M. J. Perkins, *J. Chem. Soc. C*, 2195 (1970).

[7] P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. II, W. A. Benjamin, New York, N. Y., 1966, p 358.

[8] V. v. Keussler and W. Lüttke, *Z. Elektrochem.*, **63**, 614 (1959).

[9] R. R. Holmes, *J. Org. Chem.*, **29**, 3076 (1964); see also R. Okazaki, T. Hosogai, E. Iwadore, M. Hashimoto, and N. Inamoto, *Bull. Chem. Soc. Jap.*, **42**, 3611 (1969).

[10] Stop H_2O_2 addition temporarily whenever 20° is reached. More rapid addition can cause accumulation of H_2O_2, leading to higher temperatures.