ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

Reactions of Radicals. Rates of Chain Transfer of Disulfides and Peroxides with the Polystyryl Radical[1,2]

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RECEIVED JANUARY 22, 1962

Previous attempts to determine whether radical displacement reactions occur by frontside or backside attack are discussed, and it is concluded that they do not provide a general, unambiguous answer. Part of the difficulty arises because SH2 reactions[6] on carbon atoms are too slow to compete with side reactions. Therefore, we have examined the reactions of radicals with peroxides and disulfides. These reactions are attractive for study since: (1) A few examples have been shown to involve SH2 reactions. (2) They are very fast. (3) Disulfides react with nucleophiles in SN2 reactions by backside attack. Therefore, the radical displacement reaction on sulfur may be compared with the SN2 reaction on sulfur, and that, in turn, with SN2 reaction on carbon. As an initial approach, the rate of reaction of disulfides with the polystyryl radical was determined. This approach was chosen since the rates can be obtained from chain transfer studies by well developed techniques. It involves the handicap, however, of not allowing proof of the site of attack. The data show that in both the SN2 reaction and in chain transfer, the rate constant smoothly decreases as hindrance around the sulfur atom is increased. However, in the chain transfer reaction, the spread of rate constants is greatly compressed. For example, in the SN2 reaction between mercaptide ions and disulfides, the ratio of the rate of reaction of methyl disulfide to *t*-butyl disulfide is about 10^6. In the chain transfer reaction this ratio is 66. Furthermore, a log–log graph of the rate constants for the SN2 reaction *versus* those for chain transfer is not a straight line. The implications of this are discussed. The transfer rate of benzoyl peroxide is 5 times that of benzoyl disulfide; that of di-*t*-butyl peroxide is 10 times that of *t*-butyl disulfide.

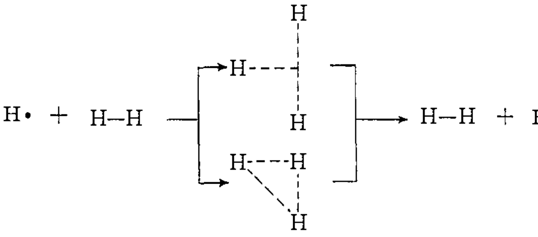
Introduction

Displacement reactions occupy a key position in the theory of chemistry. Ionic nucleophilic reactions, SN2 reactions, involve backside attack.[4] Recently it has been found that SE2 reactions frequently involve frontside attack.[5] The stereochemistry of displacement reactions by radicals, SH2 reactions,[6] is unknown, despite elegant and sophisticated studies.

Theoreticians[7,8] have been able to show that the lowest lying state on the potential energy surface for the reaction of hydrogen atoms with hydrogen molecules is linear. It involves backside attack, therefore, eq. 1.

$$\text{H}\cdot + \text{H–H} \longrightarrow [\text{H}\cdots\text{H}\cdots\text{H}] \longrightarrow \text{H–H} + \text{H}\cdot \quad (1)$$

Frontside attack, involving the triangular transition state in eq. 2A or in eq. 2B, requires more energy.



(2A)

(2B)

Unfortunately, conclusions from the theoretical treatment of more complex reactions are uncertain due to the mathematical difficulties involved. For example, some workers[9] have concluded that the reaction of chlorine atoms with hydrogen molecules involves a linear transition state, whereas others[10–12] believe it is triangular.

The first experimental study of an SH2 reaction is that of Ogg and Polanyi.[13] They found that optically active *sec*-butyl iodide racemizes when heated in the gas phase at 200–280°. They concluded that the mechanism is

$$d\text{-R–I} \longrightarrow d,l\text{-R}\cdot + \text{I}\cdot \quad (3)$$

$$\text{I}\cdot + d\text{-R–I} \longrightarrow l\text{-R–I} + \text{I}\cdot \quad (4)$$

Equation 4 was proposed to be a backside SH2 displacement. The possibility was not satisfactorily eliminated, however, that a radical attacks the alkyl iodide giving a radical which racemizes.[14b]

$$\text{I}\cdot + d\text{-R–I} \longrightarrow d\text{-R}\cdot + \text{I}_2 \quad (5)$$

$$d\text{-R}\cdot \rightleftarrows l\text{-R}\cdot \quad (6)$$

$$d,l\text{-R}\cdot + \text{I}_2 \longrightarrow d,l\text{-R–I} + \text{I}\cdot \quad (7)$$

Attempts by subsequent workers[14] to choose between these two possibilities have revealed the difficulties involved, and an unambiguous choice has not been made. Herrmann and Noyes,[14b] however,

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[1] Presented in part to the Organic Division of the American Chemical Society: Abstracts of Papers, Chicago, Ill., Sept. 3–8, 1961, p. 72-Q.

[2] Supported in part by grant RG-9020 from the National Institute of Health, for which we wish to express our thanks.

[3] National Science Foundation Undergraduate Research Participant, Summer, 1961; Undergraduate Research Assistant, 1961–1962, on grant PU-0623 from the Research Corporation.

[4] A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

[5] S. Winstein, T. G. Traylor and C. S. Garner, *J. Am. Chem. Soc.*, **77**, 3741 (1955); H. B. Charman, E. D. Hughes and C. Ingold, *J. Chem. Soc.*, 2530 (1959); F. R. Jensen, *J. Am. Chem. Soc.*, **82**, 2469 (1960); D. J. Cram and P. Haberfield, *ibid.*, **83**, 2354 (1961).

[6] Eliel has suggested use of the terms SH1 and SH2 for homolytic reactions, analogously to SN1 and SN2 for nucleophilic reactions; E. L. Eliel, in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 142.

[7] Conclusions are summarized in S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 87–91, 115.

[8] (a) H. Eyring and M. Polanyi, *Z. physik. Chem.*, **12B**, 279 (1931); (b) I. Shavitt, *J. Chem. Phys.*, **31**, 1359 (1959); (c) R. E. Weston, *ibid.*, **31**, 892 (1959).

[9] K. S. Pitzer, *J. Am. Chem. Soc.*, **79**, 1804 (1957).

[10] Reference 7, pp. 222–228.

[11] J. L. Magee, *J. Chem. Phys.*, **8**, 677 (1940).

[12] For experimental attempts to resolve this problem, see: J. Bigeleisen and M. Wolfsberg, *ibid.*, **23**, 1535 (1955); J. Bigeleisen, F. S. Klein, R. E. Weston and M. Wolfsberg, *ibid.*, **30**, 1340 (1959).

[13] R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, **31**, 482 (1935).

[14] (a) C. C. Price and M. Schwarcz, *J. Am. Chem. Soc.*, **62**, 289 (1940); D. Clark, H. O. Pritchard and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 2633 (1954); (b) R. A. Herrmann and R. M. Noyes, *J. Am. Chem. Soc.*, **78**, 5764 (1956).

have been able to limit the mechanistic possibilities.

Recently Noyes and his students[15] have reported an elegant determination of the rates of exchange of a series of alkyl iodides with I_2^{131}. They studied the reactions in the liquid phase, both degassed and in the presence of oxygen. They reason that if oxygen is present, it will compete with iodine for radicals; *i.e.*, eq. 7 will compete with eq. 8.

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (8)$$

They find that the rate of exchange is affected very little by oxygen, and conclude that very little of the exchange occurs by eq. 5, 6 and 7, and most occurs by eq. 9 and 10.

$$I_2^* \longrightarrow 2I\cdot^* \qquad (9)$$

$$I\cdot^* + RI \longrightarrow I\cdot + RI^* \qquad (10)$$

They believe eq. 10 is a Walden inversion by iodine atoms. Their data has a disturbing feature, however. They find the following relative rate sequence[16]: methyl 1.0, isopropyl 29, neopentyl 2.4. It is difficult to conceive of attack on carbon in which methyl iodine reacts at the slowest rate.[17]

Russian workers[18] have reported that organometallic compounds containing asymmetric alkyl groups transfer from one metal atom to another with retention, implying frontside attack. There is no surety, however, that radical processes are involved.

Wolfgang and his students have studied the reaction of recoil tritium atoms from nuclear reactions with organic compounds. They find[19] that tritium atoms react with optically active 2-butanol to replace the hydrogen atom attached to the asymmetric carbon atom with 91 ± 6% retention. The attack is unambiguously from the frontside. The generality of the result is unknown, however, since these "hot" atoms react having 2 to 10 e.v. of kinetic energy.[19]

It is apparent that the stereochemistry of the SH2 displacement by complex organic radicals is not known. Part of the difficulty appeared to be that radical displacements on carbon do not compete with other possible reactions, *e.g.*, hydrogen or halogen abstraction. Therefore, we have examined the reactions of radicals with disulfides and peroxides. Several features of S–S and O–O bonds make them attractive for study.

(1) Radicals cleave disulfides at the S–S bond and by a reaction that could be a direct displacement.

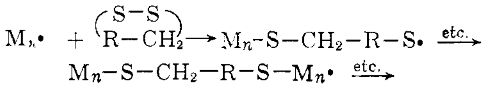
$$M\cdot + RS\text{–}SR \longrightarrow M\text{–}SR + RS\cdot \qquad (11)$$

When polymers are formed in the presence of disulfides, their rate of growth is unchanged, but their molecular weight is lowered.[20,21] Furthermore, the transfer process puts an RS group at each end of the polymer.[22,23]

$$RSM_n\cdot + RSSR \longrightarrow RSM_nSR + RS\cdot \qquad (12)$$

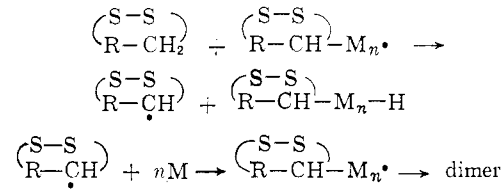
$$RS\cdot + nM \longrightarrow RSM_n\cdot \qquad (13)$$

If a cyclic disulfide is used, the rate of polymerization is nearly unchanged, but up to 18 sulfur atoms are incorporated into the polymer.[22,24]



(15)

This implies that S–S bond cleavage is involved; if hydrogen abstraction were occurring, only 2–4 sulfur atoms would be incorporated per molecule.

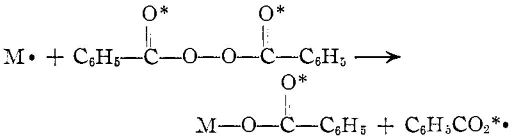


(16)

(17)

(2) Cleavage of S–S and O–O bonds by radicals is extremely fast, and therefore competes with other possible radical reactions.

(3) In the cleavage of benzoyl peroxide by various radicals, O^{18}-labeled carbonyl oxygen has been shown to retain its identity.[25]



$$M\cdot + C_6H_5\text{—}\overset{\overset{O^*}{\|}}{C}\text{—}O\text{—}O\text{—}\overset{\overset{O^*}{\|}}{C}\text{—}C_6H_5 \longrightarrow M\text{—}O\text{—}\overset{\overset{O^*}{\|}}{C}\text{—}C_6H_5 + C_6H_5CO_2^*\cdot \qquad (18)$$

The mechanism probably involves an SH2 reaction on the peroxide oxygen, and it is reasonable to suppose that other peroxides also react with radicals by an SH2 mechanism.

(4) The SN2 reaction of disulfides occurs by backside attack analogously to Walden inversion in carbon compounds. Fava, Iliceto and Camera[26,27] have convincingly demonstrated that SN2 reactions on sulfur and carbon decrease in rate by similar amounts as backside hindrance is increased. The effect of backside hindrance for the radical displacement on sulfur, therefore, may be compared with that obtained for the SN2 reaction on sulfur, and that, in turn, with the SN2 reaction on carbon. Either of the latter two re-

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[15] J. E. Bujake, M. W. T. Pratt and R. M. Noyes, *J. Am. Chem. Soc.*, **83**, 1547 (1961).

[16] Rate constants given are those determined in the presence of oxygen, which should favor a direct displacement. The degassed runs have approximately the same rate profile.

[17] See, *e.g.*, ref. 4, table 5. Furthermore, formulation of the alkyl iodide reaction as in eq. 5 is supported by comparison of the relative rates obtained by Noyes with those observed by F. W. Evans, R. J. Fox and M. Szwarc, *J. Am. Chem. Soc.*, **82**, 6414 (1960), for the reaction

$$RI + CH_3\cdot \longrightarrow R\cdot + CH_3I$$

They find that the relat ve rates are: R = Me, 1; Et, 4; *i*-Pr, 19.3; *t*-Bu, 37.

[18] O. A. Reutov, T. P. Karpov, E. V. Uglova and V. A. Malyanov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 1311 (1960); *C. A.*, **54**, 23637*e* (1960).

[19] M. Henchman and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2991 (1961).

[20] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

[21] W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[22] A. V. Tobolsky and B. Baysal, *J. Am. Chem. Soc.*, **75**, 1757 (1953).

[23] R. M. Pierson, A. J. Costanza and A. H. Weinstein, *J. Polymer Sci.*, **17**, 221 (1955).

[24] W. H. Stockmayer, R. D. Howard and J. T. Clarke, *J. Am. Chem. Soc.*, **75**, 1756 (1953).

[25] E. H. Drew and J. C. Martin, *Chemistry & Industry*, 925 (1959); D. B. Denney and G. Feig, *J. Am. Chem. Soc.*, **81**, 5322 (1959); W. Doering, K. Okamoto and H. Krauch, *ibid.*, **82**, 3579 (1960).

[26] A. Fava and A. Iliceto, *ibid.*, **80**, 3478 (1958).

[27] A. Fava, A. Iliceto and E. Camera, *ibid.*, **79**, 833 (1957).

actions may be used as models for backside attack.

Experimental

Chemicals.—Liquids were purified by repeated fractional distillation until gas phase chromatography showed a single peak using an F and M model 609 instrument with flame ionization detector, programmed at 18°/min. from 50° to 300°, and a 2-ft. Silicon rubber column. Impurities are believed to be less than 50 p.p.m. **Methyl disulfide**, Eastman Kodak Co., b.p. 111.2–111.5°; **propyl disulfide**, Eastman Kodak Co., b.p. 90.5° (11 mm.); **isopropyl disulfide**, Aldrich Chem Co., b.p. 63.0° (11 mm.); **butyl disulfide**, Eastman Kodak Co., b.p. 118.8° (20 mm.) and 71° (9 mm.); **isobutyl disulfide**, Eastman Kodak Co., b.p. 105.5° (20 mm.) and 89.0° (9 mm.); ***sec*-butyl disulfide**, Columbia Chemical Co., b.p. 106° (9 mm.) (darkens in the light); ***t*-butyl disulfide**, Eastman Kodak Co., 86° (20 mm.); **butyl sulfide**, Eastman Kodak Co., 151°; ***t*-butyl sulfide**, Aldrich Chemical Co., 151°; ***t*-butyl peroxide**, Lucidol, 62.5° (119 mm.). **Styrene** was stored over white Drierite for 24 hours to remove inhibitor,[28] then distilled; b.p. 50° (20 mm.). **Benzoyl disulfide** colors if heated in solvents. It is best purified as follows: 25 g. of Aldrich Chemical Co. benzoyl disulfide was dissolved in 350 ml. of acetone and filtered. All but 50 ml. solvent was blown off and decanted. The recovered solid was recrystallized first from 150 ml. of ethanol mixed with 150 ml. of ethyl acetate, then from 300 ml. of ethanol, and finally from 120 ml. of ethanol mixed with 120 ml. of ethyl acetate. This yields about 40% recovery of pure white platelets, m.p. 131.2–132.2°. **2,2-Dimethylbutane** was Phillips research grade, 99.99%.

Runs.—Runs were done in ampoules prepared by constricting a neck half-way down a 25 × 200 mm. ignition tube. Materials were weighed into the ampoules, which were then connected to a vacuum line by a rubber stopper. The ampoule was immersed in liquid air, evacuated to 0.2 mm., pressured with nitrogen, and the contents melted to de-air. The cycle was repeated twice more; the ampoules were then frozen once more and sealed off under vacuum.

Polymerizations were carried out by immersing the ampoules under a light-opaque oil held at 60.00 ± 0.001°. They were carried to 10–15% conversions. Ampoules were opened and % conversion determined by weighing 0.2–0.5 g. of the mixture onto a tared piece of aluminum foil, placing the foil under an air jet on an open hot-plate, and reweighing when all the styrene monomer had evaporated (about 30 min). This procedure proved faster than isolating the entire polymer and just as reproducible. Yield was independent of the aliquot size. Pure styrene gave the correct rate[28] of thermal polymerization, 0.10%/hr., and the method is therefore thought to be accurate.

Degree of polymerization, $\bar{P}$, was obtained by weighing 30 mg. of the polymer into a 25-ml. volumetric flask, diluting with dried benzene at 30.00 ± 0.02°. Flow times were measured in Cannon–Ubbelohde viscometers and were converted to specific viscosities (kinetic energy corrections were negligible), using $\eta_{sp} = (t - t_0)/t_0$. Intrinsic viscosities were calculated from the equation of Gregg and Mayo.[29]

$$[\eta] = [(1 + 1.5\eta_{sp})^{1/2} - 1)]/0.75C_v \qquad (19)$$

And the inverse of the degree of polymerization from[30]

$$1/\bar{P} = (6.2275 \times 10^{-4})/[\eta]^{1.37} \qquad (20)$$

The values obtained for $1/\bar{P}_0$ for pure styrene at 60° averaged 1.16×10^{-4}, which agrees with previously reported values.[28,31]

Theory of Chain Transfer.—The molecular weight lowering produced by the presence of a transfer agent can be related[32] to the ratio of the rate at which the polymeric radical attacks the transfer compound relative to the monomer. The equation, if the transfer agent is not an initiator, is

$$1/\bar{P} = 1/\bar{P}_0 + C\,((\mathrm{T})/(\mathrm{M})) \qquad (21)$$

Where $C = k_{tr}/k_p$, T is the transfer agent, M is the monomer, and parentheses indicate moles/liter. The rate constants are for the reactions

$$\mathrm{M}_n\cdot + \mathrm{T} \xrightarrow{k_{tr}} \mathrm{M}_n\text{—}\mathrm{T} + \mathrm{T}'\cdot \qquad (22)$$

$$\mathrm{T}'\cdot + n\mathrm{M} \xrightarrow{\text{fast}} \mathrm{T}'\text{—}\mathrm{M}_n\cdot \qquad (23)$$

$$\mathrm{M}_n\cdot + \mathrm{M} \xrightarrow{k_p} \mathrm{M}_{n+1}\cdot \qquad (24)$$

A graph of $1/\bar{P}$ *vs.* the mole ratio (T)/(M) gives C. Since the propagation rate constant k_p is known for styrene,[20] the absolute values of k_{tr} may be calculated; at 60°, $k_{tr} = 145C$ sec.$^{-1}$ M^{-1}.

Transfer Agents Which Are Also Initiators.—If T acts as an initiator as well as a transfer agent, a more complex treatment is necessary.[33] The molecular weight lowering produced by transfer and by initiation must be separated. None of the sulfur compounds studied here increases the rate of the polymerization of styrene at 60° in the dark.[34] The peroxide, di-*t*-butyl peroxide, is an initiator and data for it will be published separately.[35] Transfer constants, however, are not sensitive to small amounts of initiation. Even benzoyl peroxide, which is a very effective initiator at 60°, gives C = 0.1 from the limiting slope of eq. 21 and 0.055 if initiation is taken into account.

Data

Table I gives the value of C obtained from a least square treatment of eq. 21, the standard deviation, and the number of runs for each compound. Table I also cites previous determinations of C. The lack of agreement is not serious; most of the values previously reported are based on a single run.

Discussion

Comparison of S_H2 and S_N2 Reactions.—Table II compares the relative rate constants for the reactions:

$$\mathrm{M}_n\cdot + \mathrm{R{-}S{-}SR} \longrightarrow \mathrm{R{-}S{-}M}_n + \mathrm{RS}\cdot \qquad (25)$$

$$\overset{*}{\mathrm{S}}\mathrm{O}_3^{=} + \mathrm{R{-}S{-}SO_3^-} \longrightarrow \mathrm{R{-}S{-}}\overset{*}{\mathrm{S}}\mathrm{O}_3^- + \mathrm{SO}_3^{=} \qquad (26)$$

$$\mathrm{R}\overset{*}{\mathrm{S}}{}^- + \mathrm{R{-}S{-}SR} \longrightarrow \mathrm{R{-}S{-}}\overset{*}{\mathrm{S}}\mathrm{R} + \mathrm{RS}^- \qquad (27)$$

$$\mathrm{I}^*\cdot + \mathrm{R{-}CH_2{-}I} \longrightarrow \mathrm{R{-}CH_2{-}}\overset{*}{\mathrm{I}} + \mathrm{I}\cdot \qquad (28)$$

$$\mathrm{Y}^- + \mathrm{R{-}CH_2{-}X} \longrightarrow \mathrm{R{-}CH_2{-}Y} + \mathrm{X}^- \qquad (29)$$

$$\mathrm{I}^- + \mathrm{R{-}CH_2{-}Cl} \longrightarrow \mathrm{R{-}CH_2{-}I} + \mathrm{Cl}^- \qquad (30)$$

In these comparisons, the atom being attacked has been varied while the substituent R is kept constant. Thus, methyl disulfide, $\mathrm{CH_3{-}\overset{\downarrow}{S}{-}(SCH_3)}$, has a sulfur atom comparably hindered to ethyl halide $\mathrm{CH_3{-}\overset{\downarrow}{C}H_2(X)}$, where the arrow indicates the site of attack and parentheses enclose the leaving group. Similarly, *t*-butyl disulfide, $t\text{-Bu}{-}\overset{\downarrow}{\mathrm{S}}{-}(\mathrm{S{-}Bu}{-}t)$, is comparably hindered to neopentyl halide, $t\text{-Bu}{-}\overset{\downarrow}{\mathrm{C}}\mathrm{H_2}{-}(\mathrm{X})$. Table II has been constructed accordingly.

Comparison of the two columns for ionic reactions in Table II illustrates the point made by Fava[26,27] the S_N2 reaction has a similar rate profile regardless of whether carbon or sulfur is being attacked. The ratio of rates for R = methyl to

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[28] P. H. Boundy, R. F. Boyer and S. M. Stoesser, "Styrene," Reinhold Publ. Corp., New York, N. Y., 1952, p. 208.

[29] R. A. Gregg and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 2373 (1948).

[30] R. A. Gregg and F. R. Mayo, *ibid.*, **75**, 6133 (1953).

[31] R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 328 (1947).

[32] F. R. Mayo, *J. Am. Chem. Soc.*, **65**, 2324 (1943); ref. 20, p. 150.

[33] F. R. Mayo, R. A. Gregg and M. S. Matheson, *ibid.*, **73**, 1691 (1951).

[34] This agrees with the findings of a considerable number of workers whose work is reviewed in ref. 21 (see in particular, T. Otsu, *J. Polymer Sci.*, **21**, 559 (1956)). Styrene, as discussed in ref. 21, is particularly insensitive to initiation by disulfides.

[35] W. A. Pryor and E. P. Pultinas, to be published.

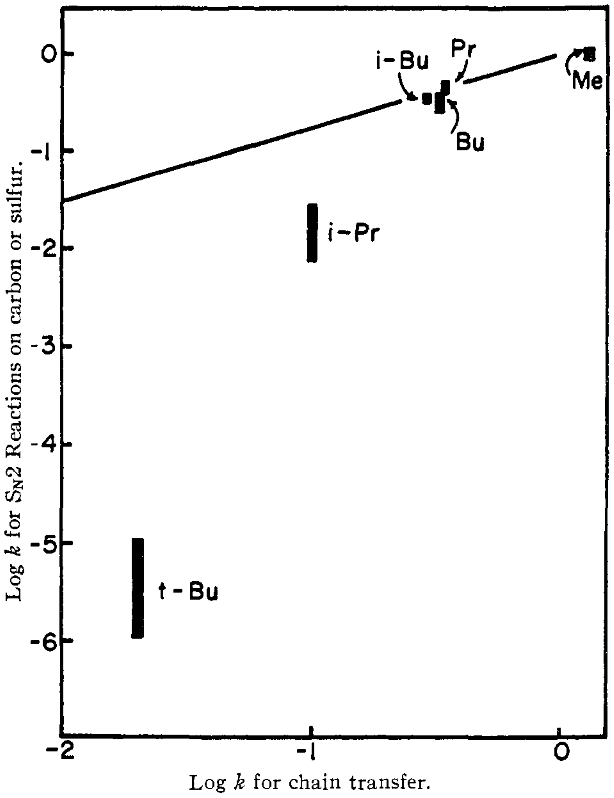
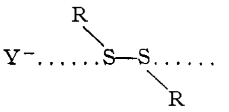
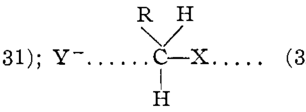


Fig. 1.—Log k for the Sn2 reaction of RCH_2-X (upper end of bar) and the Sn2 reaction of RS–X (lower end of bar) *versus* the log of the rate constant for chain transfer to RSSR.

R = *t*-butyl is 10^5 for carbon and similar for sulfur. The ratio for R = methyl to R = isopropyl is 30 for carbon and 140 for sulfur. This close correspondence implies that ions attack a disulfide along the axis of the S–S bond (eq. 31), just as ions attack alkyl halides along the axis of the C–X bond (eq. 32). In both cases the transition state involves 3 atoms in a straight line.



$$Y^- \cdots\cdots \overset{R}{S}-\underset{R}{S}\cdots\cdots \quad (31);$$

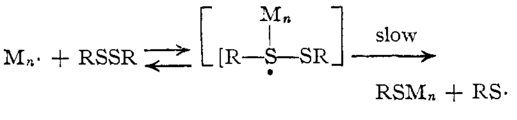


$$Y^- \cdots\cdots \overset{R\ H}{C}\underset{H}{}-X\cdots\cdots \quad (32)$$

The rate pattern for the transfer reaction at a sulfur atom may now be compared with that for either of the two ionic reactions (see Table II). In the transfer reaction (eq. 25) as well as in the Sn2 reactions (eqs. 26, 27, 29 and 30) the rate decreases continuously as the R group is made more bulky. However, the total range is much less for the transfer reaction than for the ionic reactions. For chain transfer, the ratio of rates for R = methyl to R = *t*-butyl is 66. Figure 1 is a log–log graph of the rate constant for chain transfer *versus* that for the ionic reactions given in Table II. The rate constants for the ionic and radical reactions do not parallel each other.

Attack of Radicals on Sulfur and Oxygen.—Table III gives the rate constants for attack of polystyryl radicals on related oxygen and sulfur compounds. Radicals attack O_2 much faster than S_8. However, the reaction with S_8 is a displacement reaction, and the reaction with O_2 is an addition. Also, S_2, which is more nearly analogous to O_2, is known to be more reactive than is S_8. Comparison of benzoyl peroxide with benzoyl disulfide, and *t*-butyl peroxide with *t*-butyl disulfide indicates that similar peroxides and disulfides react at similar rates. In both pairs, the peroxide is attacked from 5 to 10 times faster than the disulfide.

Several assumptions are involved, however, in making these comparisons. The carbonyl oxygen maintains its identity in the cleavage of benzoyl peroxide and, since oxygen cannot accommodate more than 8 electrons, bond-breaking must accompany bond-making. This comparison assumes that the carbonyl oxygen also maintains its identity in the reaction of benzoyl disulfide. This should be confirmed experimentally. The comparison also assumes that the displacement on sulfur does not involve prior addition with expansion of sulfur's electronic octet



$$M_n\cdot + RSSR \rightleftarrows \left[\begin{array}{c} M_n \\ | \\ [R-\underset{\bullet}{S}-SR] \end{array}\right] \xrightarrow{\text{slow}} RSM_n + RS\cdot \quad (33)$$

i.e., the assumption is that the displacement on benzoyl peroxide and disulfide involves similar mechanisms. The only evidence at present is the similarity of the rate of the reactions; this could be due to a fortuitous cancellation of opposing factors.

(2) Reaction of *t*-butyl peroxide or disulfide may involve appreciable hydrogen abstraction as well as attack on oxygen or sulfur (see below). The comparison of their total reaction rates is only

Table I

Chain Transfer Constants at 60°

Compound	n[a]	$C \times 10^4$[b]	Std. dev.[c] $\sigma \times 10^4$	$C \times 10^4$ lit.[d]
Disulfides				
Methyl	12	94.0	0.203	
Propyl	12	23.4	.199	
i-Propyl	12	6.60	.115	
Butyl	14	23.78	.488	120,[e] 68[f]
i-Butyl	11	20.37	.302	
s-Butyl	11	4.38	.496	<50[g]
t-Butyl	11	1.42	.197	<50[g]
Benzoyl	14	107	.336	<50,[g] 1100[f]
Phenyl	..	..	..	600[g]
Benzyl	..	..	..	100,[l,i] 300[h]
Monosulfides				
Butyl	18	21.8	0.578	41[j]
t-Butyl	10	250	3.12	
Peroxides				
t-Butyl	..	13[k]	..	
Benzoyl	..	..	..	550[l,m]
Misc.				
2,2-Dimethylbutane	13	0.43	0.16	

[a] Number of runs. [b] $C = k_{tr}/k_p$. [c] Standard deviation of least squares line of eq. 21. [d] Previously determined values of C; note that some are not at 60°. [e] At 60°; ref. 22. [f] At 99°; V. A. Dinaburg and A. A. Vansheidt, *J. Gen. Chem. USSR (Eng. Transl.)*, **24**, 839 (1954). [g] At 50°; A. J. Costanza, R. J. Coleman, R. M. Pierson, C. S. Marvel, and C. King, *J. Polymer Sci.*, **17**, 319 (1955). [h] At 50°; ref. 23. [i] At 60°; R. A. Gregg and F. R. Mayo, *J. Am. Chem. Soc.*, **75**, 3530 (1953). [j] At 100°; private communication from E. Perry, Monsanto Chemical Co. [k] At 60°; unpublished data of W. A. Pryor and E. P. Pultinas. [l] At 60°; ref. 33. [m] W. Cooper, *J. Chem. Soc.*, 2408 (1952).

TABLE II

COMPARISON OF THE RATE CONSTANT FOR SN2 REACTIONS AND RADICAL REACTIONS ON CARBON AND ON SULFUR

Nature of reacn. R in R_2S_2 or RCH_2X	Attack on sulfur: Radical, eq. 25 Chain transfer[a]	Attack on sulfur: Ionic, eq. 26, 27 SN2	Attack on carbon: Radical, eq. 28 Iodine atom exch.[f]	Attack on carbon: Ionic, eq. 29 SN2[d]	Alkyl halide
Me	1.36	1.0[b]	1.0	1.0	Ethyl
Et	..	0.50[b]	11.0	0.4	Propyl
Pr	0.34	..	..	.4	Butyl
i-Pr	.096	0.007[b]	..	.03	*i*-Butyl
Bu	.34	0.26[c]	..	.4	Amyl
i-Bu	.30	..	..	.4[e]	3-Methyl-1-butyl
sec-Bu	.064	..	..	..	2-Methyl-1-butyl
t-Bu	.020	6×10^{-6}[b]	2.4	10^{-5}	Neopentyl
C_6H_5	8.7	0.94[c]	..	12×10^4	Benzyl
$C_6H_5CH_2$	1.4	..	..	..	Phenylethyl
C_6H_5CO	1.63	..	..	5×10^4[e]	Phenacyl

[a] Rate constants for chain transfer in sec.$^{-1}$ M^{-1}, (*i.e.*, 145 × *C*); calculated from Table I. [b] RS–SO_3^- exchange with $SO_3^=$ in water at 25°; ref. 26. [c] RS–SR exchange with RS^- in methanol at 25°; ref. 27. The value for R = *t*-butyl for this reaction is 0.1×10^{-6}. [d] Generalized SN2 reaction; ref. 4. The value for R = Bu is extrapolated. [e] RCH_2Cl reaction iodide ion in acetone at 60°, eq. 30. The value for phenacyl is extrapolated from 0°; J. B. Conant and R. E. Hussey, *J. Am. Chem. Soc.*, **47**, 476 (1925). [f] RCH_2I reaction with iodine in hexachlorobutadiene at 160°; ref. 15.

TABLE III

RATE CONSTANTS FOR THE REACTION OF POLYSTYRYL RADICALS WITH SULFUR AND OXYGEN COMPOUNDS

Compound	k_{tr}, sec.$^{-1}$ M^{-1}	*T*, °C.
Oxygen O_2	10^8	50[a]
Sulfur, S_8	3×10^4	81[b]
Benzoyl peroxide	8.0	60
Benzoyl disulfide	1.69	60
t-Butyl peroxide	0.19	60
t-Butyl disulfide	0.020	60

[a] At 1 atm. oxygen pressure; the reaction greatly depends on oxygen pressure. F. R. Mayo, *J. Am. Chem. Soc.*, **80**, 2465 (1958); also see L. Bateman, *Quart. Revs.*, **8**, 147 (1954). [b] P. D. Bartlett and D. S. Trifan, *J. Polymer Sci.*, **20**, 457 (1956).

TABLE IV

MODEL COMPOUNDS FOR ESTIMATING THE TRANSFER CONSTANT OF *t*-BUTYL DISULFIDE

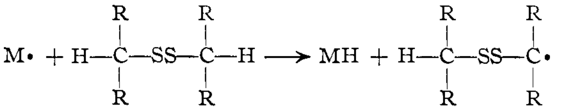
Compound	$C \times 10^4$[a]
Heptane	0.42[b]
$(CH_3)_3CCH_2CH_3$	0.43
Butyl sulfide	21.8
t-Butyl sulfide	250

[a] At 60°. [c] Ref. 31.

valid if the fraction of the attack which is not hydrogen abstraction is similar for both compounds. Further examination of this problem, and the study of other peroxides, is in progress.

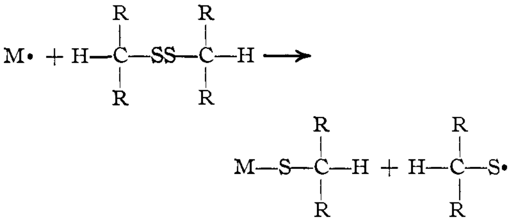
Site of the Attack.—The transfer constant measures the total rate of attack of radicals on the substrate and does not in any way specify the site of attack. As discussed in the Introduction, cycloalkyl disulfides, primary and secondary alkyl disulfides and aryl disulfides very probably react by displacement on sulfur (eq. 25). It is frequently assumed that attack by radicals on *t*-butyl peroxide or disulfide does not occur on the oxygen or sulfur atom since these atoms are thought to be too hindered.[36-39] Attack is thought to occur on a hydrogen atom instead (eq. 34 below). It is reasonable to assume that hydrogen abstraction competes for a larger percentage of the total reaction as the sulfur or oxygen atom becomes more hindered; some attack, however, probably does occur on the sulfur or oxygen. We need an estimate of the fraction of the total attack which occurs on the sulfur atom in isopropyl and *t*-butyl disulfide.

Product analysis can give these data. The product from attack on hydrogen is a hydrocarbon.



$$\mathrm{M\cdot + H{-}\underset{R}{\overset{R}{C}}{-}SS{-}\underset{R}{\overset{R}{C}}{-}H \longrightarrow MH + H{-}\underset{R}{\overset{R}{C}}{-}SS{-}\underset{R}{\overset{R}{C}}\cdot} \qquad (34)$$

Attack on sulfur produces a sulfide.



$$\mathrm{M\cdot + H{-}\underset{R}{\overset{R}{C}}{-}SS{-}\underset{R}{\overset{R}{C}}{-}H \longrightarrow M{-}S{-}\underset{R}{\overset{R}{C}}{-}H + H{-}\underset{R}{\overset{R}{C}}{-}S\cdot} \qquad (35)$$

When polymeric radicals are used, the end-groups cannot be determined with sufficient accuracy to measure this product distribution. Therefore, we are attempting to repeat this study using monomeric radicals.

As an approximation, we attempted to estimate the fraction of the total attack which occurs on the sulfur atom in *t*-butyl disulfide by use of model compounds. Table IV gives the data. The ideal hydrocarbon model for *t*-butyl disulfide would be *t*-$BuCH_2CH_2Bu$-*t*. It is not available, however, and *t*-$BuCH_2CH_3$, which should have a similar transfer constant, was used in its place. The transfer constant for this branched hydrocarbon is

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(36) Although methyl ethyl ether is a major product from the decomposition of methyl *t*-amyl peroxide, it has been assumed to arise from a termination reaction, not an SH2 reaction by ethyl radicals; J. H. Raley and D. O. Collamer, *J. Am. Chem. Soc.*, **74**, 1606 (1952).

(37) Chlorine atoms give an SH2 reaction on *t*-butyl peroxide, but apparently on hydrogen; G. Archer and C. Hinshelwood, *Proc. Roy. Soc.* (*London*), **261A**, 293 (1961).

(38) *t*-Butyl cumyl ether is a major product of the decomposition of *t*-butyl phenyldimethylperacetate, but it was assumed to arise from a cage reaction rather than an SH2 reaction by cumyl radicals; P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).

(39) L. H. Slaugh, *ibid.*, **83**, 2734 (1961), could not detect *t*-butyl *n*-butyl ether as a product of the reaction of *t*-butyl peroxide with 1-iodobutane.

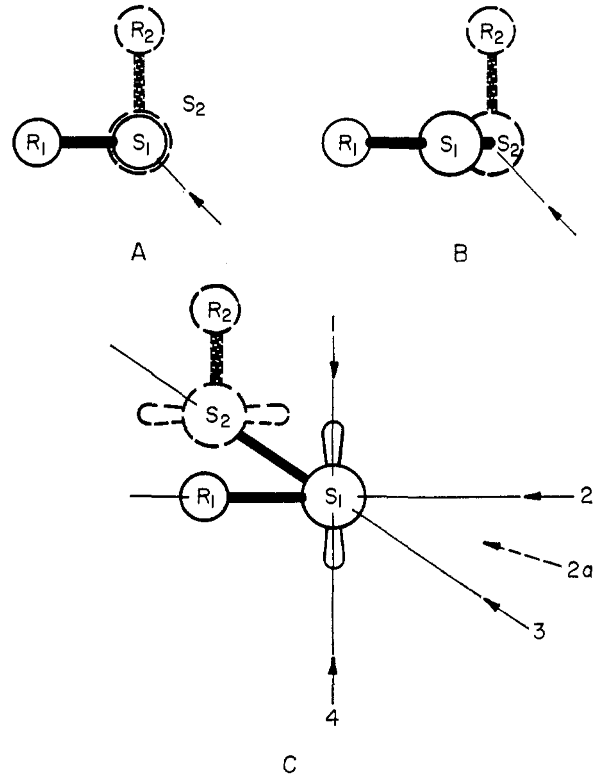
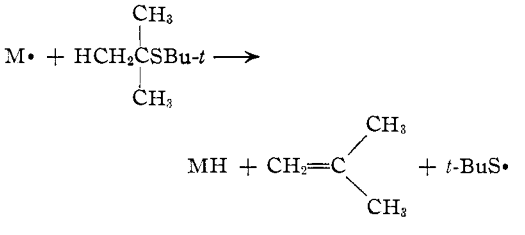


Fig. 2.—Possible directions for attack on a disulfide by a radical.

nearly identical with that of heptane. If either of these two hydrocarbons is taken as a model, *t*-butyl disulfide would be predicted to react about 0.4/1.42, or 28%, by hydrogen abstraction (see Table I) and the remainder by attack on sulfur. On this basis hydrogen abstraction would be predicted to be too slow to compete with attack on sulfur for any of the other disulfides. Unfortunately this answer cannot be accepted, since monosulfide models exhibit entirely unpredictable behavior. Butyl monosulfide has a transfer constant about equal to that of butyl disulfide, but *t*-butyl monosulfide has a transfer constant 10-fold larger. Perhaps this monosulfide reacts as



$$\text{M}\cdot + \text{HCH}_2\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}\text{SBu-}t \longrightarrow \text{MH} + \text{CH}_2{=}\text{C}\begin{smallmatrix}\text{CH}_3\\ \text{CH}_3\end{smallmatrix} + t\text{-BuS}\cdot \quad (36)$$

Regardless of the mechanism involved, this unexpectedly large transfer constant makes it clear that the study of model compounds will not suffice and that the product studies are necessary.

Conclusions.—The data of Table I show that the rate of attack on a disulfide by a polystyryl radical decreases as the sulfur is more hindered. The only data for comparison are those of Noyes,[15] in which the reaction of iodine with alkyl iodides was found to follow the reverse trend. That reaction can be formulated as attack on the iodide as in eq. 5. If it is, then ionic contributions to the transition state might explain the observed rate pattern.[17]

$$\text{R-I} + \text{I}\cdot \longrightarrow [\text{R:I}\cdot\text{I} \longrightarrow \text{R}^{+}\cdot\text{I:I}^{-}]$$

Figure 1 can be used to predict the transfer rate which should be observed in order for the transfer reaction to parallel the SN2 reaction. The transfer rate for isopropyl would have to be 0.1 to 0.01 as fast and that for *t*-butyl 10^{-5} to 10^{-7}. If the rate of hydrogen abstraction were subtracted from the total transfer rate for these two compounds, then the radical reaction and the SN2 reactions might parallel each other. For this to be true, 1 to 10% of the attack must occur on sulfur in isopropyl disulfide and about 1 part in 10^6 in *t*-butyl disulfide.

Backside SN2 attack implies a high sensitivity to backside hindrance, and neopentyl compounds react very slowly. Comparable models for SE2 frontside attack indicate that it is much less sensitive to hindrance of this type.[5] For example, cleavage of alkyl mercuric iodides, RHgI, by aqueous acids has the pattern[40]: Me 1.00, Pr 0.22, *i*-Pr 0.13, *t*-Bu 0.008; and cleavage of alkyl mercuric bromides by $HgBr_2$ has the pattern[41]: Me 1.00, Et 0.3, neopentyl 0.3. In exchange of alkyl groups between silanes, larger effects are observed.[42] However, the expectation seems supported that in reactions involving comparable energetic requirements, attack from the front is retarded less in *t*-butyl and neopentyl compounds than is attack from the rear. At present, this radical reaction more nearly parallels frontside attack. However, as discussed, the effect could be due to a compensating hydrogen abstraction reaction, and product studies will be necessary to correct for this.

Model for the SH2 Reaction.—Disulfides and peroxides have a dihedral angle near 90° and a valence angle near 105°.[43] Pauling has suggested[44] this favored conformation is due to minimization of repulsion between non-bonding electrons in p-orbitals on adjacent sulfur atoms, but other explanations are equally sound.[45] Figure 2 shows a disulfide in this conformation. Radical attack could be: (1) on the mid-point of the S–S bond, or (2) on a sulfur atom.

Figures 2A and 2B illustrate the preferred direction for attack on the bond; even in the case of R = *t*-butyl, this direction has very low steric hindrance.

If the attack is on a sulfur atom, four directions

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[40] M. M. Kreevoy and R. L. Hansen, *J. Am. Chem. Soc.*, **83**, 626 (1961).

[41] E. D. Hughes and H. C. Volger, *J. Chem. Soc.*, 2359 (1961).

[42] G. A. Russell and K. L. Nagpal, *Tetrahedron Letters*, 421 (1961). The reaction $2RSi(CH_3)_3 \rightarrow Si(CH_3)_4 + R_2Si(CH_3)_2$ involves two substrate molecules in the transition state, and therefore, F-strain effects will be accented. Equation 27 also involves two substrate molecules, and that may be the explanation for its slowness relative to eq. 26 (see footnote *c* to Table II). However, Fava has subsequently found that eq. 27 is catalyzed by oxygen and may not be as simple as shown, and the rate constants given for eq. 27 may be too large (unpublished work by Fava, Iliceto and Paron).

[43] (a) Reference 21; (b) S. C. Abrahams, *Quart. Revs.*, **10**, 407 (1956).

[44] L. Pauling, *Proc. Natl. Acad. Sci. U. S.*, **35**, 495 (1949).

[45] Reference 43; E. Cartmell and G. W. A. Fowles, "Valency and Molecular Structure," Academic Press, Inc., New York, N. Y., 1956, pp. 170–175.

must be considered, and they are indicated in Fig. 2C. Direction 3 is at the backside of the S–S bond, the bond which is cleaved, and is therefore the 3-atoms-in-a-line, "Walden inversion" direction. Direction 1 is down on one lobe of the lone-pair p-orbital, 4 is up toward its other lobe, 2 is backside to the C–S bond. Models show that the hindrance to attack increases in the order: direction $2 < 3 \sim 4 < 1$. Direction 2, the least hindered one, may be as little hindered as is attack on the S–S bond. However, attack from this direction gives a product, M—SR, with a 180° MSR angle, and this angle is actually 105°. Since sulfur has d-orbitals available for bonding, compromise directions are possible. The best direction for attack on the sulfur atom may be midway between 2 and 3; *i.e.*, from a direction that bisects the R–S–S valence angle. The optimum directions for attack are, therefore, the compromise direction 2a, and on the midpoint of the S–S bond. Both would be expected to show much less response to backside hindrance than the SN2 direction.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH AND DEVELOPMENT DIVISION, SCHERING CORPORATION, BLOOMFIELD, N. J.]

Photolysis of Nitrite Esters in Solution. I. Photochemistry of *n*-Octyl Nitrite

BY PETER KABASAKALIAN AND EDWARD R. TOWNLEY

RECEIVED MARCH 4, 1961

Complete photolysis of *n*-octyl nitrite in heptane has been found to give a 30% yield of 4-nitroso-1-octanol dimer, 2% yield of *y*-nitrosoheptane dimer and 13% yield of *y*-nitrosoheptane·4-nitroso-1-octanol dimer. The effects of photolysis solvent and temperature, concentration of *n*-octyl nitrite and oxygen upon the total yield of nitroso dimers have been studied. In the presence of oxygen, a 50% yield of *n*-octyl nitrate has been obtained.

Introduction

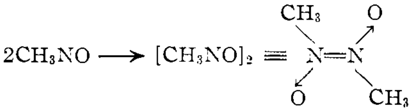
In the past, the photolysis studies of alkyl nitrites have been restricted to the obtaining of *qualitative* data on the *vapor* phase photolysis of alkyl nitrites. *t*-Butyl nitrite vapor photolysis was studied extensively by Thompson and Dainton,[1] Coe and Doumani,[2] Tarte,[3] and Gowenlock and Trotman.[4,5]

The principal product of the vapor phase photolysis of *t*-butyl nitrite is the *trans* isomer of the dimer of nitrosomethane. The formation of this product has been explained by reactions 1–4, which involve nitroso dimer formation by an *alkoxy radical decomposition mechanism* (reaction 2).

$$(CH_3)_3CONO + h\nu \longrightarrow (CH_3)_3CO\cdot + NO \quad (1)$$

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2CO + CH_3\cdot \quad (2)$$

$$CH_3\cdot + NO \longrightarrow CH_3NO \quad (3)$$



$$2CH_3NO \longrightarrow [CH_3NO]_2 \equiv \begin{matrix} CH_3 & & O \\ & \diagdown \; \nearrow & \\ & N{=}N & \\ & \swarrow \; \diagdown & \\ O & & CH_3 \end{matrix} \quad (4)$$

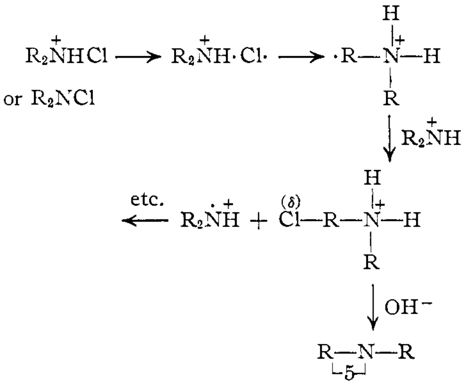
The only other tertiary nitrite studied has been *t*-amyl nitrite.[3,5] Tarte[3] has shown that ultraviolet radiation of wave lengths shorter than 330 mμ is required for the production of nitroso products.

Primary and secondary nitrites having straight chain lengths of up to five carbon atoms have also been photolyzed in the vapor phase,[5] but product analyses have been limited to the verification of the presence of the nitroso dimer moiety by ultraviolet spectrophotometry.

Although Gray and Williams[6] in their review article calculated $\Delta H = -8.5$ kcal. mole^{-1} for the internal hydrogen abstraction reaction 5 expected for long chain derivatives, rearrangements of this

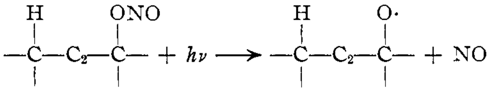
$$RCH_2(CH_2)_nCH_2O\cdot \longrightarrow \dot{R}CH(CH_2)_nCH_2OH \quad (5)$$

type have not been in fact demonstrated.[6] However, the isoelectric analog of alkoxyl radicals, $R_1R_2N\cdot$, undergoes internal hydrogen abstraction in the Hofmann-Loffler–Freytag reaction studied by Wawzonek[7] and Corey.[8]



$$\begin{array}{l} R_2\overset{+}{N}HCl \longrightarrow R_2\overset{+}{N}H\cdot Cl\cdot \longrightarrow \cdot R{-}\underset{\large R}{\overset{\large H}{\overset{|+}{\underset{|}{N}}}}{-}H \\ \text{or } R_2NCl \\ \qquad\qquad\qquad\qquad\qquad \Big\downarrow R_2\overset{+}{N}HCl \\ \xleftarrow{\text{etc.}} R_2\overset{\cdot\,+}{N}H + \overset{(\delta)}{Cl}{-}R{-}\underset{\large R}{\overset{\large H}{\overset{|+}{\underset{|}{N}}}}{-}H \qquad (6) \\ \qquad\qquad\qquad\qquad\qquad \Big\downarrow OH^- \\ \qquad\qquad\qquad\qquad\qquad \underbrace{R{-}N}_{5}{-}R \end{array}$$

Recently Barton,[9] *et al.*, have reported the formation of a hydroxy nitroso dimer as a direct result of the photolysis of the nitrite of 6β-hydroxycholestanyl acetate in benzene *solution* using filtered ultraviolet radiation (λ > 330 mμ) which did not work for Tarte.[3] The production of the nitroso dimer can be explained by reactions 7–10,



$$-\underset{|}{\overset{\overset{\large H}{|}}{C}}-C_2-\underset{|}{\overset{\overset{\large ONO}{|}}{C}}- + h\nu \longrightarrow -\underset{|}{\overset{\overset{\large H}{|}}{C}}-C_2-\underset{|}{\overset{\overset{\large O\cdot}{|}}{C}}- + NO \quad (7)$$

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(1) H. W. Thompson and F. S. Dainton, *Trans. Faraday Soc.*, **33**, 1546 (1937).

(2) C. S. Coe and T. F. Doumani, *J. Am. Chem. Soc.*, **70**, 1516 (1948).

(3) P. Tarte, *Bull. Soc. Roy. Sci. Liege*, **22**, 226 (1953).

(4) B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 4190 (1955).

(5) B. G. Gowenlock and J. Trotman, *ibid.*, 1670 (1956).

(6) P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959).

(7) S. Wawzonek and T. P. Culbertson, *J. Am. Chem. Soc.*, **81**, 3367 (1959).

(8) E. J. Corey and W. R. Hertler, *ibid.*, **82**, 1657 (1960).

(9) D. H. R. Barton, J. M. Beaton, L. E. Geller and M. M. Pechet, *ibid.*, **82**, 2640 (1960).