Polar and Solvent Effects in the Cleavage of *t*-Alkoxy Radicals

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The homolytic decomposition of various tertiary alkyl hypochlorites in carbon tetrachloride has been examined. The β scission of the intermediate *t*-alkoxy radicals was determined by quantitative analysis of the mixture of alkyl chlorides. This method, involving intramolecular competition, yields the relative rates of formation of alkyl radicals from the fragmentation of *t*-alkoxy radicals. These rates are compared with those obtained earlier from the nonchain decomposition of peroxides. Together, these results provide support for the assumptions made in the kinetic treatment. For primary radicals, the relative rates of cleavage decrease in the order: ethyl > γ,γ-dimethylbutyl > *n*-propyl, *n*-butyl > isobutyl > neopentyl ≫ methyl. The rates are slightly dependent on the structure of the alkoxy radical. The effect of structure of the alkyl moiety on the rate is reminiscent of carbonium ion type reactions. Hyperconjugative effects in the transition state for β scission are proposed. The roles of solvent in complexing and hydrogen bonding the alkoxy radicals and in the solvation of the transition state for cleavage are discussed.

Tertiary alkoxy radicals undergo a variety of free-radical reactions in solution. A kinetically second-order hydrogen transfer is the most common reaction (eq. 1). Other transformations include β scission[1]

$$R_3CO\cdot + SH \longrightarrow R_3COH + S\cdot \qquad (1)$$

to form an alkyl radical and ketone (eq. 2) and intra-

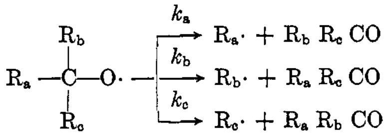
$$CH_3CH_2CH_2CH_2(CH_3)_2CO\cdot \longrightarrow CH_3CH_2CH_2CH_2\cdot + (CH_3)_2CO \qquad (2)$$

molecular hydrogen transfer[2,3] to generate an isomeric hydroxyalkyl radical (eq. 3). The latter reactions in

$$CH_3CH_2CH_2CH_2(CH_3)_2CO\cdot \longrightarrow CH_3\dot{C}HCH_2CH_2(CH_3)_2COH \qquad (3)$$

solution have been commonly considered to be first order. Pressure dependence and the unimolecularity of the cleavage of *t*-butoxy radical in the gas phase have been discussed.[4]

The relative rates of formation of alkyl radicals can be determined *directly* from the fragmentation of unsymmetrical *t*-alkoxy radicals (eq. 4).[5] These rates



$$R_a\!-\!\overset{R_b}{\underset{R_c}{C}}\!-\!O\cdot \left\{\begin{array}{l} \xrightarrow{k_a} R_a\cdot + R_b\,R_c\,CO \\ \xrightarrow{k_b} R_b\cdot + R_a\,R_c\,CO \\ \xrightarrow{k_c} R_c\cdot + R_a\,R_b\,CO \end{array}\right. \qquad (4)$$

have also been evaluated from intermolecular comparisons by employing a competing hydrogen transfer (eq. 1) as a monitoring reaction.[6] Walling and Padwa found that relative cleavage rates obtained by the direct and indirect methods differ. They attributed this discrepancy to the inconstancy of hydrogen transfer rate constants and of steric interactions with variations in the structure of the alkoxy radical. Thus, for quantitative determination the *direct* evaluation of the relative cleavage rates represents the more reliable method.

The β cleavage of tertiary alkoxy radicals is a convenient method of studying structural effects in the homolysis of carbon–carbon bonds. Qualitatively, the relative ease of ejection of an alkyl radical from the fragmentation of *t*-alkoxy radicals decreases in the order: tertiary > secondary > primary > methyl.[6,7] Effects of ring size and strain and other variables on these rates have also been examined.

In an earlier study, unsymmetrical *t*-alkoxy radicals were generated from the thermolysis of dialkyl peroxides and the reduction of alkyl hydroperoxides with reducing metal ions.[5] In the presence of hydrogen donors the radicals were converted to alkanes. Relative rates of formation of *n*-alkyl radicals were determined by analysis of the mixture of alkanes.

Alkoxy radicals are formed as intermediates in the photoinduced decomposition of *t*-alkyl hypochlorites.[8] The relevant reactions involved in this sequence are 4 and 5. The direct determination of cleavage rates, k_a, k_b, and k_c, depends on the analysis of the mixtures

$$R_i\cdot + R_a(R_b)(R_c)COCl \longrightarrow R_iCl + R_a(R_b)(R_c)CO\cdot \qquad (5)$$

of alkyl chlorides. The two direct methods of examining the rates of cleavage of alkoxy radicals differ kinetically. Peroxides as sources of alkoxy radicals involve nonchain processes, in contrast to the efficient free-radical chain decomposition of alkyl hypochlorites.[8a] From both sources the direct determination of cleavage rates depends on the assumptions that alkanes (from peroxide) and alkyl chlorides (from hypochlorites) are formed in rapid, nondiscriminating steps, 1 and 5, respectively. The methods also demand that alkyl radicals are not fractionated by extraneous reactions, such as, combination, disproportionation, etc.

In this paper we wish to establish that alkoxy radicals generated from peroxide yield the same fragmentation patterns as those derived from alkyl hypochlorites. In addition, a thorough study of *primary alkyl* substituents would aid in discerning the relative importance of the factors influencing alternative fragmentation paths, *i.e.*, the importance of the stability of the ejected radical and product ketone and the role of strain in the reactant alkoxy radical. Solvent studies should shed some light on the nature of the transition state, the degree to which the carbon–carbon bond is broken, and the contribution from ionic structures.

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(1) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

(2) F. D. Greene, *et al.*, *J. Am. Chem. Soc.*, **83**, 2196 (1961); C. Walling and A. Padwa, *ibid.*, **83**, 2207 (1961).

(3) M. Akhtar and D. H. R. Barton, *ibid.*, **83**, 2213 (1961); P. Kabasakalian, *et al.*, *ibid.*, **84**, 2711, 2718 (1962).

(4) H. Hershenson and S. W. Benson, *J. Chem. Phys.*, **37**, 1889 (1962).

(5) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1193 (1962).

(6) C. Walling and A. Padwa, *ibid.*, **85**, 1593 (1963).

(7) F. D. Greene, *et al.*, *J. Org. Chem.*, **28**, 55 (1963).

(8) (a) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108, 6113 (1960); (b) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

TABLE I

HOMOLYTIC DECOMPOSITION OF ALKYL HYPOCHLORITES IN CARBON TETRACHLORIDE

	Alkyl hypochlorite, $R_a(R_b)(R_c)COCl$			Temp.,	ROCl,[a]	Relative % RCl[b]		Total RCl,[c]	Relative rates,[d]			
	R_a	R_b	R_c	°C.	*M*	R_bCl	R_cCl	%	R_c/R_b	$E_c - E_b$[e]	$E_H - E_b$[f]	A_b/A_c[g]
I	CH_3	C_2H_5	*n*-C_3H_7	0	0.726	63.9	36.1	33.4	0.565	0.66	−0.50	0.45
				25		61.4	38.6	35.3	0.629			
				40		60.3	39.7	36.4	0.659			
II	C_2H_5	C_2H_5	*n*-C_3H_7	0	0.597	74.4	25.6	67.4	0.688[h]	0.55	−1.5	0.53
				25		72.7	27.3	72.3	0.750[h]			
				40		71.9	28.1	75.3	0.783[h]			
III	*n*-C_3H_7	C_2H_5	*n*-C_4H_9	0	1.21	43.5	27.7	20.3[i]	0.638[j]	0.63	−3.5[k]	0.48
				25		40.9	29.4	31.1	0.720			
				40		39.8	29.4	38.6	0.738			
IV	CH_3	C_2H_5	*n*-C_4H_9	0	1.08	65.9	34.1	9.87	0.519	0.79	−3.4	0.46
				25		63.0	37.0	15.4	0.587			
				40		61.7	38.3	20.0	0.621			
V	C_2H_5	C_2H_5	*n*-C_4H_9	0	1.16	76.9	23.1	21.3	0.600[h]	0.90	−3.8	0.32
				25		74.5	25.5	32.4	0.690[h]			
				40		73.0	27.0	41.4	0.741[h]			
VI	CH_3	C_2H_5	*i*-C_4H_9	0	1.07	69.9	30.1	34.8	0.431	1.10	−1.4[l]	0.30
				25		66.0	34.0	41.8	0.516			
				40		64.2	35.8	44.2	0.575			
VII	CH_3	C_2H_5	Neo-C_5H_{11}	0	0.910	72.4	27.6	71.9	0.382	0.63	−0.5[m]	0.82
				25		70.3	29.7	72.3	0.420			
				40		69.4	30.6	70.5	0.441			
VIII	CH_3	C_2H_5	*sec*-C_4H_9	0	0.956	1.1	98.9	95.3	91.1	−2.2	−1.2	0.62
				25		1.5	98.5	94.5	63.9			
				40		1.8	98.2	94.2	54.3			
IX	CH_3	*i*-C_4H_9	*n*-C_4H_9	0	0.973	42.7	57.3	18.3	1.34	−0.50	−3.3	1.9
				25		44.4	55.6	25.1	1.25			
				40		45.6	54.4	28.8	1.20			
X	CH_3	*i*-C_4H_9	Neo-C_5H_{11}	0	0.513	52.4	47.6	82.6	0.909	0.35	−0.8	0.63
				25		53.2	46.8	83.9	0.881			
				40		54.4	45.6	84.7	0.838			
XI	CH_3	*i*-C_4H_9	γ,γ-$(CH_3)_2C_4H_7$	0	0.770	32.2	67.8	40.0	2.11	−1.0	−2.8	3.0
				25		35.6	64.4	48.8	1.81			
				40		37.5	62.5	52.3	1.67			

[a] Molarity of alkyl hypochlorite. [b] Only traces of methyl chloride were observed. [c] Total β-scission products observed. [d] Molar ratio of alkyl chloride products; probable error (standard deviation), ±2%. [e] Difference in activation energies in kcalories per mole; probable error, ±5%. [f] Difference in activation energy for internal hydrogen abstraction (H) and ethyl or isobutyl cleavage (b). [g] Ratio of pre-exponential factors. [h] Corrected for statistical factor. [i] Per cent *n*-C_3H_7Cl (III), 28.8 (0°), 29.7 (25°), 30.8. [j] R_a/R_b (III), 0.662 (0°), 0.726 (25°), 0.773 (40°). [k] $E_H - E_a$ (III) = −4.1 kcal./mole. [l] b = ethyl. [m] Maximum value, determined at 0 and 25° only.

Results and Discussion

A series of unsymmetrical hypochlorites listed in Table I were prepared from the alcohols in carbon tetrachloride solutions. The conversion to alkyl hypochlorite was determined iodometrically. In all cases, it was not less than 85% and it was usually greater than 92%. Aliquots were pipetted into glass tubes and the contents were thoroughly degassed by the standard freeze–thaw method. The decompositions were conducted in a thermostated water bath and induced photolytically.

The decomposition of a *t*-alkyl hypochlorite [$R_a(R_b)(R_c)COCl$] proceeding *via* the *t*-alkoxy radical [$R_a(R_b)(R_c)CO\cdot$] can exhibit three fragmentation patterns (eq. 4 and 5). The yields of alkyl chloride and ketone as products will depend on the relative rates of the respective first-order β-scission processes, k_a, k_b, and k_c. If it is assumed that the liberated alkyl radicals only yield alkyl chloride (eq. 5),[9] the ratio of rate constants is given by eq. 6. Similar expressions are applicable to k_c. The incursion of other reactions such as hydrogen transfer (eq. 1) and rearrangement (eq. 3) which destroy alkoxy radicals does not effect these values of relative rates. Values for the relative rates were based on the yields of alkyl halides rather than those of the ketones. The ketone is more likely lost by subsequent chlorination (either heterolytically or homolytically) than the less reactive alkyl halide. In fact, chlorinated ketones have been reported as products in similar systems.[7] However, when *n*-butyl chloride was deliberately added to a solution of methylethylpropylcarbinyl hypochlorite (I), it was recovered quantitatively after photolysis.

$$\frac{k_a}{k_b} = \frac{R_aCl}{R_bCl} = \frac{R_bCOR_c}{R_aCOR_c} \qquad (6)$$

The relative ratios of β-scission products from I were also independent of initial hypochlorite concentrations (0.5–1.5 *M*), although the yields of β-scission products varied slightly with concentration (See Table IX in the Experimental Section). These ratios were invariant when decompositions were carried out in the presence of acetone. Moreover, the same values were obtained when the decompositions were interrupted at intermediate conversions.

Effect of the Structure of the Alkyl Radical.—The relative rates of cleavage of alkyl radicals from *t*-alkoxy radicals obtained by intramolecular (direct)

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[9] A. Zavitsas, *J. Org. Chem.*, **29**, 3086 (1964).

TABLE II

RELATIVE INTRAMOLECULAR RATES OF CLEAVAGE OF ALKYL GROUPS FROM *t*-ALKOXY RADICALS AT 25°

Radical	Observed relative rate[a]		Peroxide[b]
$CH_3\cdot$	<0.005[c]	...	0.003
$CH_3CH_2\cdot$	1.0[d]	1.94 (VI)	1.0[d]
$CH_3CH_2CH_2\cdot$	0.63 (I), 0.74 (II, III)	...	0.65
$CH_3CH_2CH_2CH_2\cdot$	0.59 (IV), 0.71 (III, V)	1.34 (IX)	0.43
$(CH_3)_2CHCH_2\cdot$	0.52 (VI)	1.0[d]	...
$(CH_3)_3CCH_2\cdot$	0.42 (VII)	0.88 (X)	...
$(CH_3)_3CCH_2CH_2\cdot$	0.93 (XI/VI)[e]	1.81 (XI)	...
$CH_3CH_2\dot{C}HCH_3$	64 (VIII)	...	...

[a] Roman numerals refer to alkyl hypochlorite (see Table I) employed. [b] Reference 5. [c] Estimated. [d] Relative rate = 1.0. [e] Derivative value (see text).

comparisons are given in Table II. These rates are somewhat dependent on the structure of the alkoxy radical. In general, the more highly substituted alkoxy radicals show less selectivity in the pattern of cleavage. Examples I and IV (see Table I) of the type $CH_3(R_b)(R_c)CO\cdot$ ($R \neq CH_3$) reveal a significantly lower relative rate than cases II, III, and V of the type $R_a(R_b)(R_c)CO\cdot$. Thus, the ethyl to *n*-butyl cleavage increases from 0.59 to 0.71 on replacing a methyl with either an ethyl or a propyl group. A similar pattern is observed in the comparison of the rates of ethyl and *n*-propyl cleavage.

The values for the relative rates of cleavage of methyl, ethyl, *n*-propyl, and *n*-butyl radicals compare favorably with those obtained earlier from peroxides.[5] The value for *n*-butyl radical from the latter study is slightly lower than that determined here. We feel that the present values are probably more representative. Both studies show unequivocally that ethyl radical separates from *t*-alkoxy radicals faster than other normal alkyl radicals. The source of the *t*-alkoxy radical, therefore, has no effect on the relative rates of cleavage.

Relative rates of cleavage can also be determined by *intermolecular* comparisons. A *derivative* ratio of rate constants (*e.g.*, k_a/k_b) is obtained by dividing one set of intramolecular rate constants (k_a/k_c) by another set (k_b/k_c). These rates are tabulated in Table III. Such an intermolecular comparison of rate constants involves two alkoxy radicals. Thus, effects due to varying steric factors and stabilities of the ketones can be compounded. The *derivative* determination of relative rates by cross comparison yields results most consistent with *direct* measurements when the two examples involve alkoxy radicals of nearly equivalent structure. Nonetheless, these variables play only a minor role since the *derivative* rates of cleavage are relatively constant, despite the divergent sources of radicals. They compare favorably with rates obtained by the direct method, as seen in Table III.

Discrepancies in relative rates calculated *via* the *direct* and *indirect* method have been observed.[6] Although it is an intermolecular comparison, the *derivative* method used here differs from the *indirect* method employed by Walling and Padwa.[6] Difficulties with assumptions concerning a bimolecular monitoring reaction are obviated, and the effect of structure of the *t*-alkoxy radical on cleavage rates is the sole important consideration.

TABLE III

COMPARISON OF DIRECT AND DERIVATIVE RELATIVE RATES OF CLEAVAGE OF ALKYL RADICALS[a]

Radicals	Direct[b]	Derivative[b]
C_2H_5:*n*-C_4H_9[c]	0.58 (IV) 0.69 (V) 0.72 (III)	0.69 (IX/VI)
C_2H_5:*i*-C_4H_9[c]	0.52 (VI)	0.47 (IX/IV) 0.55 (IX/V) 0.57 (IX/III)
C_2H_5:neo-C_5H_{11}[c]	0.42 (VII)	0.45 (X/VI)
n-C_4H_9:*i*-C_4H_9[d]	1.25 (IX)	1.14 (IV/VI) 1.33 (V/VI) 1.39 (III/VI)

[a] From *t*-alkoxy radicals at 25°. [b] Roman numerals refer to *t*-alkyl hypochlorite (see Table I). [c] Calculated using rate of ethyl radical = 1.0. [d] Calculated using rate of isobutyl radical = 1.0.

The best values for the relative rates of cleavage of various primary alkyl radicals are tabulated in Table IV irrespective of alkoxy radical. Those obtained by Hoare and Waters[10] from the oxidation of tertiary alcohols by cobaltic ions are also listed.

TABLE IV

SUMMARY OF RELATIVE RATES OF CLEAVAGE OF PRIMARY ALKYL RADICALS FROM *t*-ALKOXY RADICALS

Radical	Hypochlorite[a]	Peroxide[b]	Alcohol + Co(III)[c]
$CH_3\cdot$	<0.005	0.003	0.01
$CH_3CH_2\cdot$	1.0	1.0	1.0
$CH_3CH_2CH_2\cdot$	0.63–0.74	0.65	0.34
$CH_3CH_2CH_2CH_2\cdot$	0.59–0.72	0.43	0.28[d]
$(CH_3)_2CHCH_2$:	0.47–0.57	...	0.17
$(CH_3)_3CCH_2\cdot$	0.42–0.45	...	...
$(CH_3)_3CCH_2CH_2\cdot$	0.92–0.94	...	...

[a] Range of values dependent on alkoxy radical; see Tables II and III. [b] Reference 5. [c] Reference 10. [d] *n*-Amyl = 0.32.

The high rate of cleavage of ethyl radical compared to other normal alkyl radicals is also manifest by the effects of further β substitution. *As the β hydrogens of the ethyl moiety are successively substituted by alkyl groups, the rate of cleavage decreases.* Thus, isobutyl departs more slowly than either *n*-butyl or *n*-propyl radical. Neopentyl is ejected slower than isobutyl as shown in Tables I and II. This order of rates is largely independent of the structure of the resultant ketone, although there is a minor variation with the structure of the ketonic product. Furthermore, the effect is contrary to that expected for an increased steric interaction caused by alkyl substitution (*vide supra*). Homologation of the neopentyl moiety generates the γ,γ-dimethylbutyl radical, which cleaves at a rate only slightly less than ethyl radical itself. Stability, rather than size, of the departing group as a principal factor in the ease of fragmentation was also deduced by Greene and co-workers.[7]

There appears to be a correlation between the number of β hydrogens on the alkyl group and its rate of cleavage. It is the same correlation as that commonly observed in reactions generating carbonium ion intermediates.[11] Stabilization of free radicals by hypercon-

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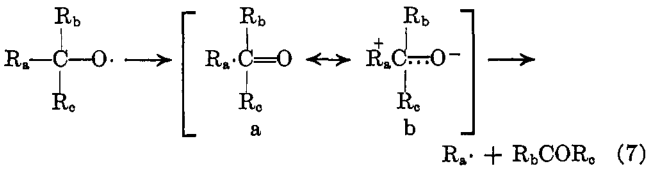
(10) D. G. Hoare and W. A. Waters, *J. Chem. Soc.*, 2552 (1964).

(11) (a) J. W. Baker, "Hyperconjugation," Oxford University Press, London, 1952; (b) M. J. S. Dewar, "Hyperconjugation," Ronald Press Co., New York, N. Y., 1962.

jugative effects have been suggested.[12] However, we propose that the hyperconjugative order in these radical cleavage reactions is due to polar effects in the transition state XII of the cleavage reaction (eq. 7).[16] We consider the degree to which polar structures such as XIIb participate in stabilizing the transition state as paralleling the importance of hyperconjugation in the alkyl moiety. This contribution decreases in the order: ethyl > *n*-propyl, *n*-butyl > isobutyl > neopentyl.



XII

There is ample evidence for polar effects in hydrogen-transfer reactions of free radicals.[13a–d] The magnitude of the effect is dependent on the radical species X.[14] Homolytic addition reactions and decomposition of peresters also show sensitivity to polar substituents.[13e–g] Atom transfers[15] involving elements other than hydrogen, such as halogen, exhibit only a very small polar effect.[16] The polar effect is related to the electron affinity and polarizability of the associated groups.

$$RH + X\cdot \longrightarrow [R\text{-}H\cdot X \longleftrightarrow R^{+}HX^{-}] \longrightarrow R\cdot + HX \quad (8)$$

Relative Energetics of the Cleavage.—The cleavage rates were determined in the temperature range between 0 and 40°. Typical variations in rates with temperature of a few hypochlorites are shown in Figure 1. The differences in activation energies, $E_c - E_b$, for cleavage of R_b relative to R_c, together with the ratios of the pre-exponential factors, A_b/A_c, obtained in this manner, are listed in Table I. In general, the relative rates are reflected in the activation energies, and there is a consistent trend for the activation energy for fragmentation to increase as one proceeds from ethyl, *n*-propyl and *n*-butyl, isobutyl, to neopentyl radical.[17] The activation energy for cleavage of γ,γ-dimethylbutyl (homologous to neopentyl) radical is closer to that for ethyl and less than that for *n*-butyl radical despite the fewer β hydrogens. Part of the lowering can be attributed to steric strain in the alkoxy radical.[18] Such an effect should be more pronounced with the more hindered neopentyl moiety. In the absence of strain, the cleavage of the neopentyl radical would then have an even higher activation energy than that observed. No consistent trend appears to be operative in the entropies of activations.

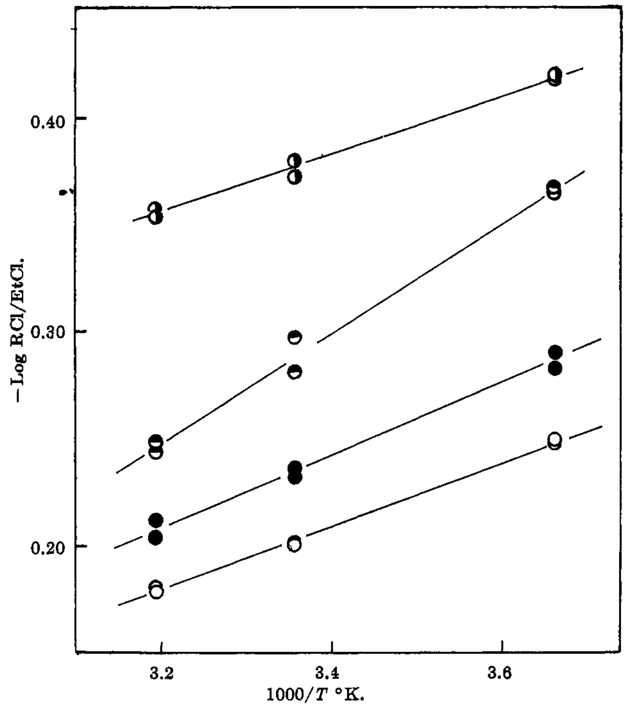


Figure 1.—Temperature dependence of cleavage rates of alkyl (R) radicals relative to ethyl radical: ○, *n*-propyl (I); ●, *n*-butyl (IV); ◓, isobutyl (VI); and ◑, neopentyl (VII).

The activation energy for the generation of alkyl radical from *t*-alkoxy radicals can be compared with that obtained by hydrogen abstraction from the alkane (eq. 9). In the gas phase, the absolute rate constants

$$RH + Y\cdot \longrightarrow R\cdot + HY \quad (9)$$

for a number of systems have been determined.[19] The relative activation energies for abstraction of hydrogen from ethane and neopentane are dependent on the abstracting radical (Y·). The difference, $E_{C_2H_6} - E_{C_5H_{12}}$, is +0.4 kcal. for methyl radical,[20] +0.1 ± 0.1 kcal. for chlorine atom,[21] and 0 for fluorine atom.[22] On the other hand, this difference is −0.75 ± 0.15 kcal. for bromine atom.[23] It reflects in part the importance of polar contributions in the transition state for bromine abstraction[24] analogous to those already discussed for alkoxy cleavage.

The Effect of Solvent.—The β-scission reaction involves a change from a polar alkoxy radical to an

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(12) (a) M. Polyani, *et al.*, *Trans. Faraday Soc.*, **37**, 377 (1941); **39**, 19 (1943); (b) ref. 11a, p. 53; see, however, ref. 11b, p. 94.

(13) (a) G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958); (b) C. Walling and B. Miller, *J. Am. Chem. Soc.*, **79**, 4181 (1957); (c) E. L. Patmore and R. J. Gritter, *J. Org. Chem.*, **27**, 4196 (1962); (d) S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964); (e) P. D. Bartlett and C. Ruchardt, *J. Am. Chem. Soc.*, **82**, 1756 (1960); (f) M. M. Martin and G. J. Gleicher, *ibid.*, **86**, 242 (1964); (g) J. I. G. Cadogan, E. G. Duell, and P. W. Inward, *J. Chem. Soc.*, 4159 (1962).

(14) G. A. Russell and R. C. Williamson, *J. Am. Chem. Soc.*, **86**, 2357 (1964); R. F. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963).

(15) E. M. Kosower and I. Schwager, *ibid.*, **86**, 5528 (1964); A. Streitwieser and C. Perrin, *ibid.*, **86**, 4938 (1964); J. K. Kochi and D. D. Davis, *Nature*, **202**, 690 (1964); *J. Am. Chem. Soc.*, **86**, 5264 (1964).

(16) C. Walling and P. J. Wagner, *ibid.*, **86**, 3368 (1964).

(17) Unfortunately, the relative activation energies of cleavage of isobutyl and neopentyl radicals obtained by the direct (example XI) and derivative (examples VI and VII) methods are not consistent. The relative activation energies by the latter method are reversed from that of the former. We believe that the value obtained by the derivative method is probably inaccurate, owing to $E_c - E_b$ (Table I) for VII being too low, although duplicate runs gave reproducible values. (Note that the yields of RCl from VII appear to go through a maximum between 0 and 40°. This was not observed in other cases.)

(18) Such strain can be considered in analogous radical reactions: C. G. Overberger, *et al.*, *J. Am. Chem. Soc.*, **76**, 6185 (1954); E. L. Eliel, "Steric Effects in Organic Chemistry," M. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y.,1956, p. 144 ff.

(19) G. C. Fettis and J. H. Knox, *Prog. Reaction Kinetics*, **2**, 1 (1964).

(20) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

(21) H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, *J. Am. Chem. Soc.*, **76**, 1201 (1954); J. H. Knox and R. Nelson, *Trans. Faraday Soc.*, **55**, 937 (1959).

(22) G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1064 (1960).

(23) G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *ibid.*, 4177 (1960).

(24) R. E. Pearson and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 3143 (1963).

equally or more polar ketonic product. The transition state XII is accordingly polar, and interaction with polar or polarizable solvent species are expected to play an important role. The effect of solvent on the cleavage of ethyl and *n*-propyl groups from methylethylpropylcarbinyloxy radical are recorded in Table V. In all solvents, with the exception of *t*-butyl alcohol, a sizeable increase in yield of β-scission products was also observed. The variations in the relative rates of cleavage with solvent change are small, but significant.

TABLE V

SOLVENT EFFECTS ON THE β SCISSION OF METHYLETHYLPROPYLCARBINYL HYPOCHLORITE[a]

Solvent (*M*)	ROCl, *M*	Relative rate, $n\text{-}C_3H_7\cdot/C_2H_5\cdot$	Cleavage, %
CCl_4	0.513, 0.612	0.560, 0.564	28.0, 31.0
Benzene (8.6)	0.513	0.628	41.3
Benzene (1.9)	0.513	0.610	35.8
Benzene (0.8)	0.513	0.577	32.1
C_6H_5CN (7.5)	0.513	0.593	48.7
C_6H_5Cl (7.6)	0.612	0.639	47.0
$(C_6H_5)_2O$ (1.9)	0.513	0.614	50.4
Naphthalene (0.8)	0.513	0.681	51.9
$Cl(CH_2)_2Cl$ (9.8)	0.612	0.585	46.8
CH_3CN (14.7)	0.612	0.603	52.3
HOAc (13.5)	0.612	0.502	63.0
$(CH_3)_3COH$ (0.33)	0.543	0.493	15.4
$(CH_3)_3COH$ (0.67)	0.543	0.475	12.4
$(CH_3)_3COH$ (1.7)	0.543	0.472	8.4
$(CH_3)_3COH$ (2.7)	0.543	0.457	6.7
CH_3CN (4.0), HOAc (1.3)	0.620	0.501	51.7
CH_3CN (4.0), $ClCH_2CO_2H$ (1.3)	0.620	0.456	58.5
CH_3CN (4.0), Cl_2CHCO_2H (1.3)	0.620	(0.506)[b]	(47)[b]
CH_3CN (4.0), Cl_3CCO_2H (1.3)	0.620	(0.516)[b]	(37)[b]

[a] At 0° in carbon tetrachloride solution. [b] Decomposition in these solvents was very slow (>30 hr. *vs.* normal <2 hr.). Therefore, there is some doubt as to the validity of these values.

The increased yields of cleavage products in aromatic solvents and acetonitrile are probably at the expense of intramolecular hydrogen abstraction[7,25] (eq. 3). Complexing[16] of the oxy radical function may serve to attenuate its activity toward hydrogen abstraction, intra- as well as intermolecular. Under these circumstances cleavage reactions are relatively more favored.

In addition to forming complexes with the alkoxy radical, these solvents stabilize the polar transition state for cleavage.[6] Walling and Wagner[16] have presented a lucid discussion of the importance of such solvation.[26] In these solvents there is corresponding loss of selectivity in the rates of ethyl and propyl cleavage as shown in Table V. Hydroxylic solvents such as carboxylic acids and *t*-butyl alcohol effect a change in the opposite direction from the aromatic solvents, and selectivity is increased relative to carbon tetrachloride. We propose that alkoxy radicals in these solvents are stabilized by hydrogen bonding. The low yield of cleavage product in *t*-butyl alcohol is due to metathesis followed by subsequent decomposition of *t*-butyl hypochlorite.

$$R_a(R_b)(R_c)COCl + t\text{-BuOH} \rightleftarrows R_a(R_b)(R_c)COH + t\text{-BuOCl} \quad (10)$$

These divergent results can be reconciled if it is assumed that complexation of the oxy function and stabilization of the polar transition states effect opposing changes in selectivity. According to Hammond's postulate,[27a] stabilization of the transition state serves to decrease selectivity since the transition state will occur earlier along the reaction coordinate.[27b] Conversely, complexation of the alkoxy radical (in one form or another) will lower its energy and delay the transition state to a region further along the reaction coordinate. In the latter case, stability of the product[28] will play a more important role in determining the rate, and greater selectivity will be observed.

The combined yields of alkyl chlorides increase with the temperature of decomposition. If it is *assumed* that this increase in yield is at the expense of the intramolecular hydrogen abstraction reaction (eq. 3) only,[29] it is possible to calculate a value for the difference in activation energies for the two processes. These were calculated as a function of the logarithm of the yield of R_bCl (R_b = ethyl or isobutyl) with respect to the rearranged product *vs.* temperature.[30] An excellent linear correlation was obtained in all cases (except example VII).[17] The difference in activation energies, $E_H - E_b$, for rearrangement and cleavage obtained in this manner, is tabulated in Table I. It shows that the activation energy for cleavage is greater than that for intramolecular hydrogen transfer. As expected, the difference is less when a primary hydrogen (−1.0 ± 0.5 kcal.) rather than a secondary hydrogen (−3.5 ± 0.5 kcal.) is involved. This probably reflects roughly the difference in energetics between abstracting a primary and a secondary hydrogen by an alkoxy radical.[31]

Experimental Section

Preparation of Alcohols.—The tertiary alcohols were prepared by the Grignard procedure from alkyl chlorides and corresponding ketones. Ketonic impurities which could not be removed from the alcohols by distillation were readily removed by treatment with Girard P reagent in methanol with acetic acid. Materials commercially obtained were purified when necessary to obtain materials giving a single peak *via* g.l.p.c. and agreeing with reported physical constants. Table VI contains a resumé of the alcohols prepared, the starting materials used, and physical constants found.

Ethylpropyl ketone was prepared by chromic acid oxidation of 3-hexanol, b.p. 122° (730 mm.). 2-Hexanol was separable from 3-hexanol by g.l.p.c.; 2-hexanone was separable from 3-hexanone.

Preparation of *t*-Alkyl Hypochlorites.—The *t*-alkyl hypochlorites were prepared from solutions of the corresponding alcohols in carbon tetrachloride by reaction with aqueous hypochlorous acid.[7] Preparations and purifications were carried out in vessels protected from light since the hypochlorites are light sensitive.

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[25] C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1597 (1963).

[26] We interpret the effects of solvation on the stabilization and on the enhancement of the polar character of the transition state for cleavage to be related phenomena. An alternative view is to consider variations in k_a/k_d or k_d to a general solvation phenomenon without relating it to the polar effect.

[27] (a) G. S. Hammond, *ibid.*, **77**, 334 (1955); (b) A. Streitwieser, *J. Org. Chem.*, **22**, 861 (1957).

[28] A. A. Zavitsas and S. Seltzer, *J. Am. Chem. Soc.*, **86**, 3836 (1964).

[29] The total cleavage and rearrangement products together constitute an excellent material balance.[6,7,17]

[30] The yield of rearranged product was taken as (100 − total RCl). In examples III, IX, X, and XI probably more than one rearranged product was formed, and $E_H - E_b$ is then a composite difference.

[31] J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 113 (1961).

TABLE VI

PREPARATION OF TERTIARY ALCOHOLS

Carbinol, $R_1(R_2)(R_3)COH$			Ketone, $R_1(R_2)CO$		Grignard, R_3MgCl	B.p., °C.		$n^{20}D$	
R_1	R_2	R_3	R_1	R_2	R_3	Found (730 mm.)	Lit. (mm.)	Found	Lit.
CH_3	C_2H_5	n-C_3H_7	CH_3	C_2H_5	n-C_3H_7	142	56 (20)[a]	1.4228	1.4231[a]
C_2H_5	C_2H_5	n-C_3H_7	C_2H_5	C_2H_5	n-C_3H_7	158–159	158–160 (733)[b]	1.4319	1.4326[c]
C_2H_5	n-C_3H_7	n-C_4H_9	C_2H_5	n-C_3H_7	n-C_4H_9	190	89 (15)[d]	1.4374	1.4378[d]
CH_3	C_2H_5	n-C_4H_9	CH_3	C_2H_5	n-C_4H_9	160–161	161–162 (763)[d]	1.4282	1.4279[d]
C_2H_5	C_2H_5	n-C_4H_9	C_2H_5	C_2H_5	n-C_4H_9	179–180	180 (733)[d]	1.4361	1.4362[d]
CH_3	i-C_4H_9	C_2H_5	CH_3	i-C_4H_9	C_2H_5	150	60–62 (16)[c]	1.4279	1.4278[c]
CH_3	C_2H_5	Neo-C_5H_{11}[e]	CH_3	C_2H_5	Neo-C_5H_{11}[e]	160–161	...	1.4348	...
CH_3	C_2H_5	*sec*-C_4H_9	CH_3	C_2H_5	*sec*-C_4H_9	150–151	150–152 (740)[c]	1.4350	1.4350[c]
CH_3	i-C_4H_9	n-C_4H_9	CH_3	i-C_4H_9	n-C_4H_9	189–190	...	1.4341	...
CH_3	i-C_4H_9	Neo-C_5H_{11}[e]	CH_3	i-C_4H_9	Neo-C_5H_{11}[e]	185–186	...	1.4370	...
CH_3	i-C_4H_9	γ,γ-$(CH_3)_2C_4H_7$[f]	CH_3	i-C_4H_9	γ,γ-$(CH_3)_2C_4H_7$[f]	205–206	...	1.4383	...

[a] F. C. Whitmore and D. E. Baderscher, *J. Am. Chem. Soc.*, **55**, 1559 (1933). [b] J. M. Church, F. C. Whitmore, and R. V. McGrew, *ibid.*, **56**, 176 (1934). [c] R. C. Huston, *et al.*, *ibid.*, **70**, 1090 (1948). [d] F. C. Whitmore and H. M. Woodburn, *ibid.*, **55**, 361 (1933). [e] 2,2-Dimethylpropyl. [f] 3,3-Dimethylbutyl.

TABLE VII

DECOMPOSITION OF METHYLETHYLPROPYLCARBINOL HYPOCHLORITE[a]

Temp., °C.[b]	Area[c]		Marker[d]	C_2H_5Cl (1.075)[f]		n-C_3H_7Cl (1.188)[f]		Total mmoles of RCl	% cleavage[g]	Rel. rate, $C_2H_5\cdot/n$-C_3H_7
	EtCl/Hex	PrCl/Hex		mmoles[e]	Rel. %	mmoles[e]	Rel. %			
0	0.521	0.324	0.1769	1.536	63.9	0.8674	36.1	2.404	33.1	1.771
0	0.554	0.346	0.1692	1.562	63.8	0.8859	36.2	2.448	33.7	1.764
25	0.513	0.357	0.1833	1.567	61.3	0.9903	38.7	2.558	35.2	1.583
25	0.487	0.336	0.1954	1.586	61.5	0.9936	38.5	2.580	35.5	1.596
40	0.460	0.335	0.1963	1.505	60.2	0.9953	39.8	2.500	34.4	1.512
40	0.461	0.334	0.2037	1.565	60.3	1.030	39.7	2.595	35.7	1.520

[a] Hypochlorite concentration 0.726 *M* in CCl_4 solution. [b] Decomposition temperature, ±0.3°. [c] Ratio of areas from gas chromatogram, C_2H_5Cl (or n-C_3H_7)/hexane marker. [d] Weight of hexane marker (grams) added to ampoule. [e] Millimoles of alkyl chloride per 10 ml. of sample, calculated: (area ratio)(marker)(calibration factor)/(mol. wt. of RCl). [f] Calibration factor (see Table VIII). [g] Calculated from millimoles of RCl and concentration of hypochlorite solution.

TABLE VIII

RELATIVE RETENTION TIMES AND CALIBRATION FACTORS OF ALKYL CHLORIDES

Compd.	Column							
	A		B		C		D	
	R.r.t.[a]	m[b]	R.r.t.[a]	m[b]	R.r.t.[a]	m[b]	R.r.t.[a]	m[b]
CH_3Cl	0.40	...	...	...	...	...	0.42	...
C_2H_5Cl	1.0	1.075	1.0	1.205	...	...	1.0	1.056
n-C_3H_7Cl	3.18	1.188	3.62	1.183	...	...	3.03	1.183
n-C_6H_{14}[c]	3.75	...	4.42	...	1.0	...	3.58	...
i-C_4H_9Cl	6.43	1.242	7.44	1.245	1.56	1.681	6.10	1.184
sec-C_4H_9Cl	...	...	...	...	...	...	6.40	1.147
CCl_4	9.50	...	11.8	...	2.05	...	9.02	...
n-C_4H_9Cl	10.8	...	12.9	1.142	...	...	10.2	...
Neo-$C_5H_{11}Cl$	...	...	14.3	1.337	...	...	...	...
γ,γ-$(CH_3)_2C_4H_7Cl$	...	...	...	...	5.21	1.447	...	...

[a] Relative retention time. [b] Calibration factor, *i.e.*, slope of weight (RCl/hexane) *vs.* area (RCl/hexane). [c] n-Hexane marker (internal standard).

The general procedure is described for methylethylpropylcarbinyl hypochlorite.

Aqueous sodium hypochlorite was prepared from an aqueous solution of sodium carbonate and 70% calcium hypochlorite (Olin Matheson HTH) by the method of Greene and co-workers.[7]

Methylethylpropylcarbinyl Hypochlorite.—A solution of 8.12 g. (0.07 mole) of methylethylpropylcarbinyl hypochlorite in 25 ml. of purified[32] carbon tetrachloride and 8.6 ml. (0.15 mole) of glacial acetic acid were added with stirring to 90 ml. of the cooled (0°) aqueous sodium hypochlorite solution (*ca.* 2.6 *M*). After stirring in the dark at 0° for 90 min., the nonaqueous layer containing the hypochlorite was separated; the aqueous layer was extracted with three 15-ml. portions of carbon tetrachloride. The combined carbon tetrachloride fractions were washed with three 20-ml. portions of 3% aqueous sodium bicarbonate and two 10-ml. portions of water and dried over sodium sulfate. The solution was used as such without further isolation, since solutions showed no OH absorption in the infrared indicating quantitative conversion. The hypochlorite concentration was determined by iodometric titration (yield, 88%).

Hyprochlorite decompositions were carried out in sealed, degassed, glass ampoules by irradiation with an incandescent lamp (15-w.) in a thermostated bath. All decompositions were carried out on two or more duplicate samples and at various hypochlorite concentrations. Completion of reaction was detected by the disappearance of the characteristic yellow color (and substantiated by iodometric analysis). The general procedure is described in detail for a representative case (Table VII).

Methylethyl-*n*-propylcarbinyl Hypochlorite.—A 10-ml. sample of a 1.01 *M* solution of the hypochlorite in CCl_4 was pipetted into a 25-ml. long-necked ampoule (aluminum foil covered), degassed by three cycles of freezing, evacuating, and thawing (closed off from the vacuum source), and sealed *in vacuo*. After decomposition was complete (1–2 hr.), the ampoule was cooled

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[32] A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1951, p. 174.

(0°), opened, and sealed with a rubber septum cap, and a known amount of *n*-hexane was introduced as an internal standard.

Decompositions carried out in solvents other than carbon tetrachloride were performed in solutions prepared by diluting a concentrated solution (2–3 *M*) of the hypochlorite in carbon tetrachloride with a carbon tetrachloride solution of the second solvent component. Chloroacetic acids required acetonitrile as a third solvent component to maintain solution of the acid component.

Quantitative analyses of reaction mixtures were carried out by g.l.p.c. techniques. The columns used for analyses of the alkyl halides were calibrated with standard solutions at the same time and under the same conditions as the unknown. The peak areas on the chromatogram for each component of both the calibration and reaction solutions were determined with a planimeter.

From the ratio of peak areas (alkyl chloride to hexane) of the calibration mixture and the amount of each component in the calibration mixture, the constant *m* could be determined for the following simple proportionality.

$$\frac{\text{weight of RCl}}{\text{weight of hexane}} = m\frac{\text{area of RCl}}{\text{area of hexane}}$$

The values of *m*, the areas from the unknown mixtures, and the amount of hexane added to the unknown were then used to calculate the amount of each component present. Reproducibility was 2–3% and experimental errors represent the spread between two or more duplicate analyses. Results are reported as average values.

The gas chromatographic columns are described below. Relative retention times for alkyl chlorides are reported in Table VIII as are the calibration factors. Product ketones were not eluted from columns A, B, and D and were much later than the alkyl chlorides from column C.

Gas Chromatographic Columns and Conditions.—The following columns were used: A, 20-ft. α-chloronaphthalene (7%), Bentone 34 (5%) on Chromosorb P (35–80 mesh) at 18° and 10 p.s.i. of N_2 carrier gas; B, same as above at 0° and 16 p.s.i. of N_2 pressure; C, 12-ft. didecylphthalate (15%), Bentone 34 (5%) on Chromosorb W-HMDS (60–80 mesh) at 70° and 10 p.s.i. of N_2 carrier gas; and D, 12-ft. α-chloronaphthalene (7%), Bentone 34 (5%) on Chromosorb P (35–80 mesh) at 25° and 10 p.s.i. of N_2 carrier gas.

Chloride Determination *via* Solvolysis and Volhard Titration.—The CCl_4 solution resulting from the hypochlorite photolysis was rinsed into a 100-ml. round-bottom flask with acetone. The CCl_4 and alkyl chlorides were removed *via* a rotary vacuum evaporator with benzene added as chaser; complete removal of carbon tetrachloride was checked by g.l.p.c. A 2 *M* sodium hydroxide–50% aqueous ethanol solution (10 ml.) and a magnetic stirring bar were added; the flask was capped (rubber septum) and heated (oil bath) at 80° for 48 hr. with stirring. The resulting solution was titrated for chloride after acidification (HNO_3) with a $AgNO_3$–NaSCN system (ferric ammonium sulfate indicator). The sum of the chloride titer and amount of alkyl chlorides (by g.l.p.c.) consistently resulted in a 98–100% accounting of chloride based on the amount of *t*-alkyl hypochlorite initially present. No ionic chloride or hydrogen chloride was formed in detectable amounts during photolysis.

TABLE IX

EFFECT OF HYPOCHLORITE CONCENTRATION ON CLEAVAGE RATES AND YIELDS[a]

Alkyl hypochlorite $R_a(R_b)(R_c)COCl$					
R_a	R_b	R_c	ROCl,[b] *M*	Relative rates,[c] R_c/R_b	Total RCl,[d] %
CH_3	C_2H_5	*n*-C_3H_7	1.01	0.635	36.2
			0.726	0.629	35.3
			0.507	0.632	34.6
			0.338	0.631	34.0
n-C_4H_9	C_2H_5	*n*-C_3H_7	1.21	0.726	31.1
			0.764	0.724	28.9
			0.382	0.727	25.0
CH_3	C_2H_5	*n*-C_4H_9	1.08	0.587	15.4
			0.539	0.577	13.5

[a] Decomposition temperature, 25 ± 0.3°. [b] Molarity of alkyl hypochlorite in CCl_4. [c] Molar ratio of alkyl chloride products. [d] Total β-scission products observed.

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Synthesis of Unsymmetrical Azoalkanes from Acylalkylhydrazones and 1,2-Dialkylhydrazines[1]

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The syntheses of various unsymmetrical azoalkanes by oxidation of 1,2-dialkylhydrazines, obtained from the lithium aluminum hydride reduction of acylalkylhydrazones, are described. The boiling points are related to those of the analogous hydrocarbons. The azoalkanes, unlike dialkylhydrazines, show no additional structure-dependent interactions. Infrared and ultraviolet absorption data are presented and the *trans*-azo stretching frequency is assigned to 1562 cm.$^{-1}$ (6.40 μ).

Azoalkanes have recently attracted renewed interest as progenitors of alkyl radicals by photolytic,[4] radiolytic,[5] and pyrolytic[6] reactions. For related studies in this laboratory it became of interest to have available azoalkanes containing differing alkyl groups in the same molecule, corresponding to the general formula, $R_aN{=}NR_b$, where R_a and R_b are not identical.[7] A search of the literature showed prior reporting of two such compounds: isopropylazo-*sec*-butane, $(CH_3)_2$-

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(2) Visiting Research Associate on leave from University of Dayton during the summer of 1962.

(3) A portion of this work is derived from theses submitted by W. A. R. (June 1960) and G. L. U. (July 1963) to the Air Force Institute of Technology in partial fulfillment of the requirements for the M.S. degree.

(4) (a) C. Steel and M. Szwarc, *J. Chem. Phys.*, **33**, 1677 (1960); (b) M. Shanin and K. O. Kutschke, *J. Phys. Chem.*, **65**, 189 (1961); (c) S. Toby, *ibid.*, **64**, 1575 (1960); (d) R. H. Riem and K. O. Kutschke, *Can. J. Chem.*, **38**, 2332 (1960); (e) B. C. Roquitte and J. H. Futrell, *J. Chem. Phys.*, **37**, 378 (1962); (f) J. A. Kerr and J. G. Calvert, *J. Am. Chem. Soc.*, **83**, 3391 (1961); (g) R. K. Lyon, *ibid.*, **83**, 4290 (1961).

(5) L. J. Stief and P. Ausloos, *J. Phys. Chem.*, **65**, 877 (1961).

(6) (a) T. A. Whatley, Ph.D. Thesis, University of Oregon, 1961; University Microfilms, Ann Arbor, Mich., L. C. No. Mic 61-2089; *Dissertation Abstr.*, **21**, 3652 (1961); (b) M. B. Neiman, V. Ya. Efremov, and Yu. Ya. Efremov, *Trudy po Khim. i Khim. Tekhnol*, **2**, 500 (1959); (c) J. B. Levy and B. K. W. Copeland, *J. Am. Chem. Soc.*, **82**, 5314 (1960).

(7) These compounds are called "unsymmetrical" azoalkanes by Chemical Abstracts Service [*Chem. Abstr.*, **56**, 44n (1962)], although there is a possibility of confusion because they are obtainable by oxidation of "symmetrical" hydrazines rather than unsymmetrical ones. These latter have two alkyl groups on the same nitrogen.