Energetics of Alkyl Radical Reactions. Competitive Abstraction of Halogens[1]

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Ethyl, isopropyl, cyclohexyl, and t-butyl radicals have been made to abstract a chlorine atom from a t-alkyl hypochlorite or a bromine atom from bromotrichloromethane in competition. In all cases the energies of activation favor bromine abstraction while the pre-exponential factor favors chlorine abstraction. The t-butyl radical abstraction of chlorine appears, mainly on the basis of a large relative entropy of activation, to proceed via a concerted mechanism to produce simultaneously another t-butyl radical and ketone. A strong solvent effect on the ratio of β-scission to hydrogen abstraction by the oxy radicals was found in CCl₃Br vs. CCl₄. The stabilization energy of the alkyl radical is quantitatively related to the extent of bond breaking in the transition state.
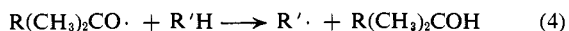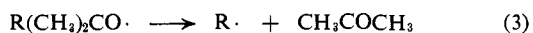
Introduction

In an attempt to discover quantitative relationships between energies of activation of a series of related free-radical reactions and stabilization energies of the radicals (i.e., resonance and hyperconjugation energies), a series of experiments was carried out, in which different simple alkyl radicals were made to react with two substrates in competition according to the general scheme outlined in eq. 1 and 2. The radicals ($R \cdot$) were

$$R \cdot + AX \longrightarrow RX + A \cdot \qquad (1)$$
$$R \cdot + BY \longrightarrow RY + B \cdot \qquad (2)$$
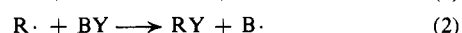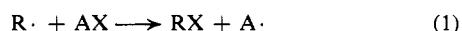
ethyl, isopropyl, cyclohexyl, t-butyl, and cyclopentenyl. The pair of substrates used were a tertiary hypochlorite (AX) and bromotrichloromethane (BY).
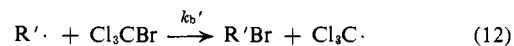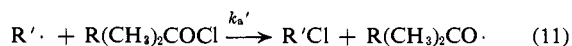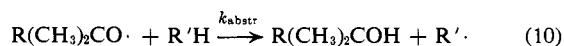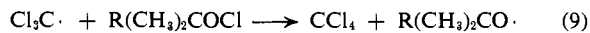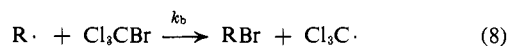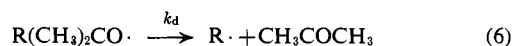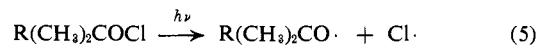
The alkyl radicals were generated in either of two ways: (a) by β-scission of the appropriate tertiary oxy radical, as in eq. 3, or (b) by abstraction of hydrogen by the oxy radical from the appropriate hydrocarbon, as in eq. 4. Cleavage of tertiary oxy radicals, formed

$$R(CH_3)_2CO \cdot \longrightarrow R \cdot + CH_3COCH_3 \qquad (3)$$
$$R(CH_3)_2CO \cdot + R'H \longrightarrow R' \cdot + R(CH_3)_2COH \qquad (4)$$

from the corresponding hypochlorites, to yield alkyl radicals and ketones, is a very convenient way of producing alkyl radicals and has been well studied and frequently used.[2-4] Alkyl groups other than methyl cleave with relative ease at the temperatures employed, and this method was used to produce ethyl, isopropyl, and t-butyl radicals. The cyclohexyl and cyclopentenyl radicals were produced by abstraction of hydrogen from cyclohexane and cyclopentene, respectively. The oxy radical is the abstracting agent and this reaction also has been well studied.[5-7]

We did not obtain an extended enough series of activation energies to provide a firm basis for the formulation of the quantitative relationships mentioned above. Our method of approach to the problem is, however, rather uncommon in that relative reactivity studies have usually been carried out with the same radical acting on a series of substrates,[5,6,8] whereas we worked with a series of different radicals acting on the same pair of substrates. The results show some interesting features and clarify some of the implications of previously published data.

As an example we will describe and discuss in detail one of the experiments in which both methods of radical formation (β-scission and hydrogen abstraction) were used simultaneously. A mixture of bromotrichloromethane (7.54 M), isopropyldimethylcarbinyl hypochlorite (0.408 M), and cyclohexane (1.55 M) was prepared. An aliquot of this mixture was placed in a Pyrex tube, degassed, sealed, and placed in a bath maintained at 73°. Another aliquot was treated in the same fashion and thermostated at 0°. Irradiation with a 250-w. incandescent light source was used to initiate the reaction after the sample had temperature equilibrated in the bath. The reaction reached completion in about 20 min. as shown by the disappearance of the yellow color of the hypochlorite. The significant reactions are shown in eq. 5-12; R = i-C₃H₇, R' = c-C₆H₁₁ in the experiments just described. The

$$R(CH_3)_2COCl \xrightarrow{h\nu} R(CH_3)_2CO \cdot + Cl \cdot \qquad (5)$$
$$R(CH_3)_2CO \cdot \xrightarrow{k_d} R \cdot + CH_3COCH_3 \qquad (6)$$
$$R \cdot + R(CH_3)_2COCl \xrightarrow{k_a} RCl + R(CH_3)_2CO \cdot \qquad (7)$$
$$R \cdot + Cl_3CBr \xrightarrow{k_b} RBr + Cl_3C \cdot \qquad (8)$$
$$Cl_3C \cdot + R(CH_3)_2COCl \longrightarrow CCl_4 + R(CH_3)_2CO \cdot \qquad (9)$$
$$R(CH_3)_2CO \cdot + R'H \xrightarrow{k_{abstr}} R(CH_3)_2COH + R' \cdot \qquad (10)$$
$$R' \cdot + R(CH_3)_2COCl \xrightarrow{k_a'} R'Cl + R(CH_3)_2CO \cdot \qquad (11)$$
$$R' \cdot + Cl_3CBr \xrightarrow{k_b'} R'Br + Cl_3C \cdot \qquad (12)$$

photochemical reaction (eq. 5) is significant only for the initiation, but hardly accounts for any of the products since all subsequent reactions are chain reactions and the chain lengths in such systems are long.[5] The ratios k_a/k_b and k_a'/k_b' can be determined from the experimentally determined ratio of alkyl chloride to alkyl bromide formed and from a knowledge of the initial concentrations of hypochlorite and bromotri-

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.
(2) C. Walling and A. Padwa, J. Am. Chem. Soc., 85, 1593 (1963).
(3) F. D. Greene, et al., J. Org. Chem., 28, 55 (1963).
(4) A. A. Zavitsas and S. Seltzer, J. Am. Chem. Soc., 86, 1265 (1964).
(5) C. Walling and B. B. Jacknow, ibid., 82, 6113 (1960).
(6) C. Walling and W. Thaler, ibid., 83, 3877 (1961).

(7) C. Walling and A. A. Zavitsas, ibid., 85, 2084 (1963).
(8) Among some recent examples: (a) R. F. Bridger and G. A. Russell, ibid., 85, 3754 (1963); (b) B. P. McGrath and J. M. Teder, Bull. soc. chim. Belges, 71, 772 (1962); (c) D. M. Tomkinson, J. P. Galvin, and J. O. Pritchard, J. Phys. Chem., 68, 541 (1964).

chloromethane. It should be recognized that we are not directly concerned with the over-all rate-determining steps in the reaction as such, i.e., β-scission of and hydrogen abstraction by the relatively stable alkoxy radicals, but rather only with the manner in which these steps distribute the final halide products between RX and R'X (*vide infra*).

The solution of the kinetic equations for our system, where one of the substrates is completely consumed, is somewhat more complicated than that encountered in the more common methods of relative reactivity determinations, where the substrates are present in excess or where they are not completely consumed at the end of the reaction.[6-8] Exact treatment of the kinetics and a much simpler approximate treatment for limiting concentration and relative rate conditions are given in the section on kinetics and product-determining relations. The Arrhenius parameters were determined in the usual fashion from the temperature dependence of the rate constant ratios.

Kinetics and Product-Determining Relations

For the general case where bromides and chlorides are formed subsequent to the β-scission and hydrogen abstraction reactions of the tertiary alkoxy radicals, i.e., in reaction equations 7, 8, 11, and 12

$$\frac{d[RCl]}{dt} = k_a[R\cdot][R(CH_3)_2COCl] \tag{13}$$

$$\frac{d[RBr]}{dt} = k_b[R\cdot][CCl_3Br] \tag{13a}$$

$$\frac{d[R'Cl]}{dt} = k_a'[R'\cdot][R(CH_3)_2COCl] \tag{14}$$

$$\frac{d[R'Br]}{dt} = k_b'[R'\cdot][CCl_3Br] \tag{14a}$$

Combination of eq. 13 and 13a yields the differential equation relating the formation of RCl and RBr

$$\frac{d[RCl]}{d[RBr]} = \frac{k_a[R(CH_3)_2COCl]}{k_b[CCl_3Br]} \tag{15}$$

A similar equation is derivable for the R' products.

Since the concentration of all radicals is at all times small

$$\Delta[CCl_3Br] = [RBr] + [R'Br] \tag{16}$$

$$\Delta[R(CH_3)_2COCl] = [RBr] + [R'Br] +$$
$$[RCl] + [R'Cl] \tag{16a}$$

By either use of the steady-state approximation for the radical concentrations or by simply considering the fate of $R(CH_3)_2CO\cdot$ undergoing β-scission or abstracting hydrogen from R'H, one may easily show

$$\frac{[R'Br] + [R'Cl]}{[RBr] + [RCl]} = \frac{k_{abstr}[R'H]}{k_d} \tag{17}$$

Since [R'H] is always much greater in the studies here described than the fraction of $R(CH_3)_2CO\cdot$ which abstracts, [R'H] is essentially constant with time. Hence, we designate $k_{abstr}[R'H]/k_d = C$ and adopt as well the following simplifying symbolism: $k_a/k_b = K$, $k_a'/k_b' = K'$, $[R(CH_3)_2COCl]_0 = B$, $[CCl_3Br]_0 = A$, $[RCl] = y$, $[RBr] = x$, $[R'Cl] = y'$, and $[R'Br] = x'$.

We now consider two special cases which cover the kinetics for all the reactions studied here.

For R = ethyl and isopropyl, where one must consider both the abstraction and scission reactions, $[CCl_3Br] \gg [R(CH_3)_2COCl]$. Hence, $[CCl_3Br]$ remains essentially constant during the reaction. From eq. 15 then

$$\frac{dy}{dx} = K\frac{[B - (1 + C)(x + y)]}{A} \tag{18}$$

This equation may be most simply integrated by transforming variables, i.e., $z = (x + y)$. Upon rearrangement of eq. 18

$$dx = dz/\left\{(1 + KB/A) - \frac{K(1 + C)}{A}z\right\} \tag{19}$$

Integration is straightforward from this point; doing so and rearranging yields

$$y = \frac{(A + KB)}{(1 + C)K}(1 - \exp(-K(1 + C)x/A)) - x \tag{20}$$

At $t \to \infty$, $B = (1 + C)(x + y)$. Introducing this relation we find

$$\frac{KB}{A}\left(\frac{1}{1 + (y/x)_\infty}\right) - \log\left(1 + K\frac{B}{A}\right) = 0 \tag{21}$$

where $(y/x)_\infty$ is the measured ratio $[RCl]_\infty/[RBr]_\infty$. Note, the $t \to \infty$ expression does not have any C dependence.

By similar derivations, the relations for the cyclohexyl products are obtainable. These are identical in form with eq. 20 and 21 with K, y, and x replaced by their primed counterparts, and $C' = 1/C$.

For R = t-butyl, the initial concentrations of CCl_3Br and $R(CH_3)_2COCl$ are similar but all oxy radicals undergo scission. Therefore

$$\frac{dy}{dx} = K\frac{[B - (x + y)]}{A - x} \tag{22}$$

which is identical with

$$\frac{dy}{dx} + \left(\frac{K}{A - x}\right)y = K\left(\frac{B - x}{A - x}\right) \tag{23}$$

This is an ordinary differential equation of the first order which upon integration yields

$$y = \left\{(B - A)(A^K - Z^K) + \frac{K}{K - 1}ZA\left(A^{K-1} - Z^{K-1}\right)\right\}A^{-1} \tag{24}$$

where now $Z = A - x$. At $t \to \infty$, $B = x + y$. Upon substitution of this identity and elimination of y we find

$$Z_\infty = {}^{K-1}\sqrt{A^K/\{(K - 1)B + A\}} \tag{25}$$

Transforming to the more convenient logarithm form and recognizing that $Z/A = 1 - \{B/A(1 + y/x)\}$

$$\log\left(1 - \frac{B}{A}\left(\frac{1}{1 + (y/x)_\infty}\right)\right) + \frac{1}{K - 1}\log\left(1 + \frac{(K - 1)B}{A}\right) = 0 \tag{26}$$

Table I. Relative Rate Constants and Activation Parameters for Alkyl Radical Abstractions of Chlorine and Bromine

Radical	$[R(CH_3)_2-COCl]_0{}^a$	$[Cl_3CBr]_0{}^a$	Temp., °C.	$[RCl]/[RBr]^b$	$k_{Cl}/k_{Br}{}^c$	$E_{Cl}{}^* - E_{Br}{}^*$, kcal./mole	(A_{Cl}/A_{Br})	$S_{Cl}{}^* - S_{Br}{}^*$, e.u.
$CH_3CH_2\cdot$	0.374	6.85	0	0.473	19.7	0.15	26	6.4
			70	0.495	20.7			
$(CH_3)_2CH\cdot$	0.408	7.54	0	0.204	8.03	0.92	44	7.5
			73	0.287	11.5			
$c\text{-}C_6H_{11}\cdot$	0.408	7.54	0	0.0324	1.22	1.14	10	4.6
			73	0.0504	1.90			
$(CH_3)_3C\cdot$	0.249	0.825	0	0.660	4.83	3.25	1930	15.0
			60	1.63	14.2			
$(CH_3)_3C\cdot$	0.264	0.297	0	1.54	4.04	3.38	2050	15.2
			60	3.66	12.4			
$c\text{-}C_5H_7\cdot$	0.656	1.30	0	0.0348	0.095	−6.91	2.8×10^{-7}	−30.0
			50	0.00485	0.013			

^{a} Initial concentrations. ^{b} Final ratio. ^{c} Ratio of rate constants for chlorine to bromine abstraction.

This equation form, modified by the primes on K, y, and x, will quickly be recognized to also hold in the cyclopentenyl studies, where essentially all the oxy radicals abstract to form $R'\cdot$.

Both eq. 21 and 26 which are transcendental in K may be conveniently solved by an iterative technique such as the Newton–Raphson method. The results reported herein were obtained by IBM 7094 processing of the experimental data by this method.

Equation 21 may be reduced in the special case where KB/A is small, i.e., $K < A/B$, to a much simpler expression for K. Expanding the log term in eq. 21 to the second order in KB/A one obtains

$$\frac{KB}{A}\left(\frac{1}{1 + (y/x)_\infty}\right) = \frac{KB}{A} - \frac{1}{2}\left(\frac{KB}{A}\right)^2 \qquad (27)$$

Since KB/A small implies $(y/x)_\infty \ll 1$

$$K \cong \frac{2A}{B}\left(\frac{y}{x}\right)_\infty \qquad (28)$$

or

$$\frac{k_a}{k_b} = \frac{[CCl_3Br][RCl]}{(^1/_2)[R(CH_3)_2COCl][RBr]}$$

One may easily show as well that for $B \ll A$ and $K - 1$ small, eq. 26 reduces through similar expansion of the log terms to eq. 28. This is to be expected from comparison with eq. 21, recognizing the latter to be derived on the basis of $B \ll A$ and to be independent of C.

Results and Discussion

An implicit assumption in this treatment is, of course, that eq. 6–12 represent all the significant reactions that occur in the experimental system. Abstraction of hydrogen by the trichloromethyl radical (eq. 29) is an important reaction in the bromination of reactive hydrocarbons by bromotrichloromethane.[9,10] The occur-

$$Cl_3C\cdot + RH \longrightarrow Cl_3CH + R\cdot \qquad (29)$$

rence of this reaction would not affect our kinetic scheme, but, in any case, it has been shown that in

(9) (a) E. C. Kooyman, R. Van Helden, and A. F. Bickel, *Proc. Koninkl. Ned. Acad. Wetenschap.*, **B56**, 150 (1953); (b) E. S. Huyser, *J. Org. Chem.*, **26**, 3261 (1961); (c) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 391 (1960).
(10) G. A. Russell and C. De Boer, *ibid.*, **85**, 3136 (1963).

systems containing hydrocarbon and both bromo-trichloromethane and t-alkyl hypochlorite reaction 29 does not occur to any significant extent.[11]

Another possibility is the formation of alkyl halides by a process such as eq. 30, where X is either bromine

$$R\cdot + XCl_2CCl \longrightarrow RCl + XCl_2C\cdot \qquad (30)$$
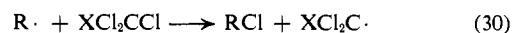
or in the cases where carbon tetrachloride was used as the solvent, chlorine. Phenyl radicals, for example, are known to abstract chlorine atoms from carbon tetrachloride.[8a] This possibility has been investigated[12] for a series of alkyl radicals, ranging in stability from benzyl to neopentyl, and carbon tetrachloride in the presence of hypochlorite labeled with Cl^{36}. The reactions were found to be the usual hypochlorite chlorinations of alkanes and aralkanes. It was determined that no significant amounts of activity appeared in the carbon tetrachloride, as would have been the case if the process shown in eq. 30 was operative; this reaction would subsequently be followed by a reaction equivalent to eq. 9. These findings can be extended to rule out alkyl chloride formation by eq. 30 for the similar case of bromotrichloromethane. Additional support for this conclusion is furnished by the absence of any reports of alkyl chlorides in the products of photoinduced brominations of alkanes with bromo-trichloromethane.[9,10]

Our scheme (eq. 6–12) further requires that the total amount of cyclohexyl halides formed be equal to the amount of alcohol formed (eq. 10). The mass balance was established. The total amount of isopropyl halides and the amount of acetone formed should be equal (eq. 6). This was also found to be so, indicating that the isopropyl and cyclohexyl halides formed are stable under the conditions of reaction and analysis.

Table I shows the results, experimental conditions, and calculated Arrhenius parameters. The values reported are the results of duplicate experiments analyzed in triplicate. The n-propyl radical was also investigated, but it is not included in the table since its behavior was identical with that of the ethyl radical.

For the first six entries of Table I the solvent was bromotrichloromethane and for the last six carbon tetrachloride. The sixth column gives the ratio of the

(11) C. Walling and A. Padwa, *J. Org. Chem.*, **27**, 2976 (1962).
(12) A. A. Zavitsas, *ibid.*, **29**, 3086 (1964).

rate constant for reactions 7 and 8, or for 11 and 12, or their equivalent. The seventh column gives the calculated difference in activation energy between abstraction of a chlorine atom from hypochlorite and a bromine atom from bromotrichloromethane by the alkyl radical. An additional comment regarding the last two entries of Table I is required. We established that allylic and benzylic bromides are unstable at the injector temperatures required for g.l.c. analysis of these products; the corresponding chlorides, however, do not decompose. The final ratio of cyclopentenyl chloride to bromide shown in column 5 was calculated from the final amounts of cyclopentenyl chloride and tertiary alcohol, as shown in eq. 31 and 32. Even

$$[R'Cl]_f + [R'Br]_f = [R(CH_3)_2COH]_f \quad (31)$$

$$\frac{[R'Cl]_f}{[R'Br]_f} = \frac{[R'Cl]_f}{[R(CH_3)_2COH]_f - [R'Cl]_f} \quad (32)$$

though we did not measure the allyl bromide directly, we are reasonably confident that eq. 31 and 32 are applicable; one cannot assume that significant amounts of allyl radicals disappear by processes other than halogen abstraction, e.g., coupling and disproportionation. In the presence of a tertiary alkyl hypochlorite or bromotrichloromethane, allyl radicals are known to give the halides in high yields.

The activation parameters for the competitive reactions of the ethyl, isopropyl, and cyclohexyl radicals were determined in bromotrichloromethane solvent, whereas those for the t-butyl and cyclopentenyl radicals were determined in carbon tetrachloride solvent in the presence of bromotrichloromethane. The possibility that this change in solvent influences the activation parameters (vide infra) was investigated in the case of the t-butyl radical; the amount of bromotrichloromethane was varied threefold with no significant change in ΔE^* and ΔS^* (Table I). This is taken to constitute a good although by no means absolute indication that such solvent effects are unimportant here.

From Table I it can be seen that for radicals not stabilized by a double bond or phenyl group in the 2-position, it is energetically more favorable to abstract bromine from bromotrichloromethane than chlorine from a tertiary alkyl hypochlorite. The pre-exponential (entropy) terms, however, favor chlorine abstraction. The combined effects favor the latter at the temperatures of interest here.

In the case of the cyclopentenyl radical, one of the competing reactions (bromine abstraction) is apparently an endothermic process.[11] We have concluded, however, that cyclopentenyl bromide is the predominant halide formed; the ratio of pre-exponential terms is very unfavorable for chlorine abstraction.

Further, while the differential activation energies for abstraction seem to vary regularly through the alkyl radical series (primary to tertiary), a rather abrupt and seemingly significant dislocation is noted in the corresponding entropy value series. The primary and secondary radicals have ΔS^* ($R \ln [A_a/A_b]$) values in the range 5–8, while for the t-butyl radical the value is 15 e.u. This abrupt increase in entropy leads one to suspect a possible change in mechanism. With the further knowledge that no dimethyl t-butyl carbinol is found upon decomposition of the precursor hypo-

chlorite, which is unique for the alkyl cases studied, one may reasonably suggest that simultaneous bond ruptures occur upon chlorine abstraction, i.e., t-butyl radical plus the hypochlorite yields in a single step t-butyl chloride, acetone, and another t-butyl radical. The stretched C–C bond here, as contrasted to the same bond in the transition states for the other alkyl hypochlorites, would result in a less ordered system and is therefore consistent with a larger activation entropy increase. It is useful to attempt a rough qualitative decomposition of the extra 7 e.u. accompanying this process. On the order of 3 e.u. may be obtained by freeing the rotation of the t-butyl group in the transition state.[13] The loss of entropy involved in fixing the Cl position relative to $R(CH_3)_2CO$, so that carbonyl orbitals are properly disposed for ketone formation, is probably compensated by the freeing of methyl rotations in the ketone. Another increment would be forthcoming from extra vibrational (in the limit, translational) freedom in the transition state. Here, we have essentially hypochlorite $\rightarrow$ acetone + t-butyl chloride (with a t-butyl radical in both the reactant and transition states canceling) compared to $R \cdot$ + hypochlorite $\rightarrow$ RCl + oxy radical in the other decomposition cases. Since the former process involves production of two species from one (in the limit) compared to two from two in the latter, an additional $\sim$2 e.u. difference may reasonably be expected in a comparison of the two decomposition processes. Finally, and qualitatively independent of whether the reaction is concerted or not, the steric effects of two t-butyl groups must also contribute to increase ΔS^*.

Our results establish more firmly some lower limits for the energy of activation for chlorine atom abstraction from t-alkyl hypochlorites by alkyl radicals. A value of 2 ± 2 kcal./mole is one of the existing estimates for abstraction by the benzyl radical.[14] We find at least 3.3 kcal./mole for the t-butyl radical; for the cyclopentenyl radical the activation energy difference found in our competitive system is of little value by itself since one of the competing processes is endothermic. If the trend established by the series ethyl, isopropyl, cyclohexyl, t-butyl, extends regularly to include the allylic and benzylic radicals, a minimum of about 5.5 kcal./mole is suggested.

In reactions of the type shown in eq. 1 and 2, the heats of reaction are given by

$$-\Delta H_1 = (-R_R + R_A) - D_{A-X} + D_{R-X} \quad (33)$$

$$-\Delta H_2 = (-R_R + R_B) - D_{B-Y} + D_{R-Y} \quad (34)$$

where R_R is the stabilization energy of the attacking radical, R_A and R_B that of the radicals produced, and the D terms are the bond energies involved.[15]

The difference, $\Delta\Delta H$ (eq. 35), is almost invariant for the series ethyl to t-butyl since the first two terms on the right-hand side are independent of the attacking radi-

$$\Delta\Delta H = -(\Delta H_1 - \Delta H_2) = (R_A - R_B) + (D_{B-Y} - D_{A-X}) + (D_{R-X} - D_{R-Y}) \quad (35)$$

(13) K. S. Pitzer and W. D. Gwinn, J. Chem. Phys., 10, 428 (1942).
(14) C. Walling and B. B. Jacknow, J. Am. Chem. Soc., 82, 6108 (1960).
(15) M. G. Evans, Discussions Faraday Soc., 2, 271 (1947), and references therein.

cal and the last term is constant within 1 kcal. for the halides of the simple alkyl groups.[16] A relationship of the Evans–Polanyi type (eq. 36), applied here can furnish some information concerning the transition

$$\Delta\Delta E^* = \alpha\Delta\Delta H = \alpha(-\Delta H_1 + \Delta H_2) \quad (36)$$

states for these reactions.

$\Delta\Delta E^*$ is the activation energy difference between reactions 1 and 2, and α is a constant, varying between zero and unity, which decreases with an increase in the reactivity of the attacking radical. Deuterium effects correlate with a similar constant in the Evans–Polanyi relationship, and this constant has also been used as a measure of bond breaking in the transition state.[17] The reactivity of the substrate is likely to affect α to some extent but for this discussion we will assume it to be nearly independent of substrate reactivity. This assumption is supported by the report that $\alpha = 0.4$ for abstraction by the phenyl radical of a series of hydrogens of greatly different reactivity.[8a] The values for ΔH in our series of reactions cannot be calculated exactly because of insufficient data for calculation of $(R_A - R_B)$, the difference in the stabilization energies of the t-alkoxy and trichloromethyl radicals relative to some common reference. This differential stabilization term is often neglected in calculating exothermicities; by relying only on the bond energy terms, we find a value of about 20 kcal./mole for $\Delta\Delta H$.[18] Substitution of this value and of the experimentally determined activation energy differences into eq. 36 leads to $\alpha = 0.0075$ for ethyl, 0.046 for isopropyl, and 0.165 for t-butyl as the attacking radical. The relation cannot be extended to cyclopentenyl since one of the competing reactions is endothermic.

Stabilization energies for simple alkyl radicals are available from electron impact measurements, $E_s(\text{Me}\cdot) = 0$, $E_s(\text{Et}\cdot) = 5$, $E_s(i\text{-Pr}\cdot) = 11$, and $E_s(t\text{-Bu}\cdot) = 16$ kcal./mole.[19] A linear relationship appears to exist between these stabilization energies and $\log \alpha$ (Figure 1). The straight line is described by eq. 37, where E_s is expressed in kcal./mole. Further data are required to definitely verify this relationship, but it appears to hold

$$\alpha = 1.9 \times 10^{-3} \, e^{0.28E_s} \quad (37)$$

over a 25-fold change in α and a threefold change in E_s. For cyclohexyl, α is 0.057 and Figure 1 would predict a stabilization energy of about 12.2 kcal./mole for this

(16) Tested with values from E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, **39**, 19 (1943).

(17) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

(18) Bond energies from the following sources: (a) T. L. Cottrell, "The Strength of Chemical Bonds," Academic Press Inc., New York, N. Y., 1954; (b) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 2; (c) ref. 15; (d) E. C. Baughan and M. Polanyi, *Nature*, **146**, 685 (1940); the same O–Cl bond strength, 44 kcal.,[14] was used for all t-alkyl hypochlorites by analogy with the constancy of the O–H bond strength in a series of t-alkyl alcohols from part d. Note well, ordinarily this type of relationship is applied to reactions where A and B in eq. 1 and 2 are similar and where the reaction of higher exothermicity has the smaller activation energy. Here, A and B are quite dissimilar which may account for the noted reversal of the reaction enthalpy–activation energy order. The comparisons subsequently made are in terms of $\Delta\Delta H$ values which are opposite in sign to those derived by usual convention. Alternatively, if $\Delta\Delta H$ is derived in the usual manner, α assumes negative values.

(19) J. L. Franklin and H. E. Lumpkin, *J. Chem. Phys.*, **19**, 1073 (1951). From $D(\text{R–H}) - D(\text{CH}_3\text{–H})$, where the methane dissociation is arbitrarily taken as standard to reflect resonance (hyperconjugation) stabilization in the other radicals. The E_s values may be as significant as reported and are taken to represent the radicals in the same configuration as they exist in the reaction solutions.
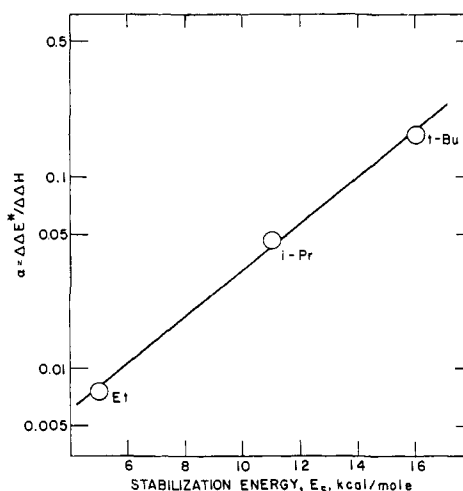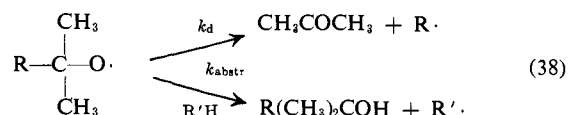
Figure 1. Log α vs. stabilization energy of R·.

radical. There are reports in recent free-radical literature of the greater lability of cyclohexane hydrogens toward abstraction by the t-butoxy radical, compared to secondary hydrogens of straight-chain hydrocarbons[6]; this "additional" reactivity toward abstraction is apparently caused primarily by the greater stabilization of the cyclohexyl radical, rather than by considerations of accessibility or other entropy effects.

The relative rates of β-scission and hydrogen abstraction were investigated in detail as a function of temperature for the oxy radical derived from isopropyldimethylcarbinyl hypochlorite. An interesting type of solvent effect was discovered. Solvent effects have been discovered in the last few years in several t-butoxy radical reactions. Small effects of aromatic solvents on the properties of t-butoxy radicals have been reported, both on selectivity and ratio of β-scission (cleavage) to abstraction,[14,20] k_d/k_{abstr} in eq. 38. The effect of complexing solvents on k_d/k_{abstr} for the t-butoxy

$$\begin{array}{c} CH_3 \\ | \\ R{-}C{-}O\cdot \\ | \\ CH_3 \end{array} \xrightarrow{\overset{k_d}{}} \begin{array}{l} CH_3COCH_3 + R\cdot \\ \\ \xrightarrow[R'H]{k_{abstr}} R(CH_3)_2COH + R'\cdot \end{array} \quad (38)$$

radical has been studied in considerable detail.[21,22] For the t-butoxy radical, the difference between the energy of activation for β-scission and for abstraction $(E_d^* - E_{abstr}^*)$ is about 10 kcal./mole in the gas phase and noncomplexing solvents and decreases in the presence of complexing solvents down to 5.9 kcal./mole in acetic acid. However, as the energy of activation for β-scission decreases because of complexing, there is a trend toward more unfavorable activation entropies for cleavage. Acetic acid solvent causes a 13-fold increase in the ratio of the pre-exponential terms, A_{abstr}/A_d.[21]

For R = isopropyl in eq. 38, $k_d/k_{abstr} = 6.15$ at 0°, 76.4 at 40°, and 109 at 70° in carbon tetrachloride as solvent and 4.65 M cyclohexane; this corresponds to $E_d^* - E_{abstr}^*$ of about 1.7 kcal./mole and A_{abstr}/A_d of about 1 $\times$ 10^{-3}. We find that for R = isopropyl in

(20) (a) G. A. Russell, *J. Org. Chem.*, **24**, 300 (1959); (b) E. L. Patmore and R. J. Gritter, *ibid.*, **27**, 4196 (1962).

(21) (a) C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **85**, 2333 (1963); (b) *ibid.*, **86**, 3368 (1964).

(22) A. A. Zavitsas and S. Seltzer, *ibid.*, **86**, 3836 (1964).

bromotrichloromethane solvent and 1.55 M cyclohexane (R'H), k_d/k_{abstr} as calculated by eq. 39 is substantially smaller. At $0°$, $k_d/k_{abstr} = 0.830$; at $73°$, $k_d/k_{abstr} = 1.507$. This corresponds to $E_d^* - E_{abstr}^* = 1.53$ kcal./mole and $A_{abstr}/A_d = 7.2 \times 10^{-2}$. Apparently, then, this solvent effect comes about not from a significant differential stabilization of the two transition states for β-scission and hydrogen abstraction, but primarily from a substantial differential effect of solvent

$$\frac{k_a}{k_{abstr}} = [R'H]\frac{[RCl] + [RBr]}{[R'Cl] + [R'Br]} \qquad (39)$$

on the corresponding entropies of activation. The oxygen atom appears to be the complexing site, from studies of solvent effects on selectivity.[21] In order for abstraction to occur, this complex must be loosened considerably with a concomitant entropy gain in the transition state. In this case complexing of the oxy radical with bromotrichloromethane favors abstraction by a factor of about 70 in the ratio of the pre-exponential terms.

Experimental

Materials. All hypochlorites were prepared from the corresponding alcohols which are commercially available materials. All reagents were distilled prior to use and purity was checked by physical constants and g.l.c. (gas–liquid chromatography).

Preparation of Hypochlorites. The hypochlorites were prepared from the corresponding alcohols essentially as in ref. 12. Briefly, chlorine was bubbled through carbon tetrachloride until a solution about 1.5 N results. The chlorine was oxidized by a 10% excess of mercuric oxide yellow with stirring for an hour, and the hypochlorous acid was extracted with ice-cold water. Yields are around 70%. The required amount of alcohol was dissolved in either bromotrichloromethane or carbon tetrachloride, and a twofold molar excess of aqueous hypochlorous acid was added. The heterogeneous system was stirred vigorously at $10°$ for 3 hr. in absolute darkness. The organic layer was separated, neutralized with 5% sodium carbonate, washed, and dried at night with only a 15-w. red light bulb for illumination. Iodometric titration showed yields invariably greater than 96%, based on the alcohol. The high yields indicated that chlorination of the alkyl group on the tertiary alcohols did not occur to any significant extent. The hypochlorites were stored in brown bottles at $-5°$. It may be worthwhile to point out here that some of these tertiary alkyl hypochlorites are stable almost indefinitely under the above mentioned storage conditions. One such hypochlorite (dimethylphenylcarbinyl) showed less than 1% decomposition in 14 months.

Competitive Reactions. The appropriate amounts of reactants and solvent were charged into Pyrex ampoules protected from light and were degassed and sealed. The ampoules were placed in constant temperature baths and, after temperature equilibration, were irradiated with a 250-w. incandescent light bulb from a distance of about 15 cm. for at least 0.5 hr. beyond the disappearance of the yellow color of the hypochlorite. Materials charged to the ampoule for each competitive experiment were as follows.

Ethyl radical: 0.374 M ethyldimethylcarbinyl hypochlorite, 1.55 M methylcyclohexane, 6.85 M bromotrichloromethane (solvent).

Isopropyl and cyclohexyl radical: 0.408 M isopropyldimethylcarbinyl hypochlorite, 1.55 M cyclohexane, 7.54 M bromotrichloromethane (solvent).

t-Butyl radical: 0.249 M t-butyldimethylcarbinyl hypochlorite, 0.825 M bromotrichloromethane, in carbon tetrachloride solvent. In another series of experiments: 0.264 M t-butyldimethylcarbinyl hypochlorite, 0.297 M bromotrichloromethane in the same solvent.

Cyclopentenyl radical: 0.656 M t-butyl hypochlorite, 1.30 M bromotrichloromethane, 2.80 M cyclopentene, 0.233 M chlorobenzene (internal standard), in carbon tetrachloride solvent.

Analyses were performed by g.l.c., mostly on dinonyl phthalate or Carbowax on KOH-washed Chromosorb-W. Compounds were identified by comparison of their retention times with authentic materials on at least two different columns. The stability of all compounds under the applied analytical conditions was checked. It was found that benzyl and cyclopentenyl bromides and bromotrichloromethane were unstable at injector temperatures above about $130°$. Thermal conductivity corrections were applied in cases where the calculations of energies of activation required the taking of sums or differences of quantities determined by g.l.c.