Such neighboring-group participation is a significant factor if the transition state of the reaction involves breaking of the carbon–hydrogen bond and consequently radical formation at the carbon atom allowing for the bridged radical to contribute to lowering the activation energy requirement. The effect is observed in the endothermic hydrogen abstraction by bromine atoms and might be expected in hydrogen atom abstraction by the thiyl radical which is also an endothermic reaction. Contribution of the bridged radical species to the hydrogen abstraction from the chlorohydrins IV and V by a chlorine atom is small. Little carbon–hydrogen bond breaking develops in the transition state of the reaction, and consequently the carbon has little radical character to allow for bridging with the β chlorine. This being the case, no advantage is obtained in the conformational requirement of positioning the chlorine anti to the abstracted hydrogen. The lack of a neighboring-group effect in the chlorohydrin reaction cannot be attributed to the inability of the chlorine, which is isoelectronic with bivalent sulfur, to form bridged radicals since such species have been reported in other systems.[5]

Experimental Section[6]

***threo*-3-Chloro-2-butanol (IV)** was prepared from *cis*-2-butene and hypochlorous acid by the general method described by Coleman and Johnstone,[7] bp 24–26° (5 mm) [lit.[8] bp 36.5–40 (14 mm)]. The ir and nmr spectra of the material were consistent with the assigned structure.

***erythro*-3-Chloro-2-butanol (V)** was prepared from *trans*-2-butene and hypochlorous acid,[7] bp 55–60° (80 mm) [lit.[8] bp 44–44.5° (16–20 mm)]. The ir and nmr spectra were consistent with the assigned structure.

***cis*-2,3-Epoxybutane (VI).**—This material was prepared both by reaction of *cis*-2-butene with *m*-chloroperbenzoic acid following the procedure of Pasto and Cumbo[9] and by elimination of hydrogen chloride from *threo*-chloro-2-butanol with potassium hydroxide in aqueous solution as described by Wilson and Lucas,[10] bp 58–59° (lit.[10] bp 59.9–60.4°).

***trans*-2,3-Epoxybutane (VII).**—This compound was prepared from *trans*-2-butene and *erythro*-3-chloro-2-butanol, respectively, by methods described in the previous experiment, bp 53.0–54.5° (lit.[10] bp 53.6–54.1°).

***threo*-3-Bromo-2-butanol (VIII).**—*cis*-2,3-Epoxybutane was added dropwise with constant stirring to an excess of 48% hydrobromic acid cooled in an ice bath. The mixture was allowed to stir for 6 hr and then neutralized with sodium bicarbonate and extracted with ether. After the ether solution was dried over anhydrous magnesium sulfate, the solvent was removed leaving a residue which on distillation gave the desired product, bp 35–38° (5.8 mm) [lit.[11] bp 48–50° (12 mm)].

***erythro*-3-Bromo-2-butanol (IX).**—*trans*-2,3-Epoxybutane gave IX when it was allowed to react with hydrobromic acid in the manner described in the previous experiments, bp 41–43° (6.2 mm) [lit.[11] bp 51–53° (12 mm)].

***threo*-3-Methylthio-2-butanol (X).**—*cis*-2,3-Epoxybutane was added dropwise to an alcoholic solution of sodium methyl sulfide (prepared from methanethiol and sodium ethoxide in absolute ethanol) at 0–5°. After the solution was stirred at room temperature for 20 hr, the resulting mixture was taken up in ether and washed repeatedly with sodium bicarbonate and saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and, after removal of the ether, distillation of the resulting residue gave the desired product (50% of theory), bp 38–39° (1.45–1.50 mm).

Anal. Calcd for $C_5H_{12}OS$: C, 50.00; H, 10.07; S, 26.70. Found: C, 50.12; H, 10.31; S, 26.12.

***erythro*-3-Methylthiol-2-butanol (XI)** was prepared in about 50% yield from *trans*-2,3-epoxybutane by the same procedure, bp 48–51° (1.35–1.50 mm).

Anal. Calcd for $C_5H_{12}OS$: C, 50.00; H, 10.07; S, 26.70. Found: C, 50.34; H, 10.22; S, 26.29.

General Procedures for Competition Reaction.—Solutions consisting of a pair of epimeric alcohols, di-*tert*-butyl peroxide (5–10 mol %), an internal standard for the gas chromatographic analyses (chlorobenzene for the 3-chloro-2-butanols and bromobenzene for 3-bromo-2-butanols and 3-methylthio-2-butanols), and acid scavenger (propylene oxide or cyclohexene oxide) were divided into several Pyrex tubes, sealed, and placed in a constant temperature bath set at 125°. Tubes were removed after several hours, by which time 25–30% of the less reactive isomer had reacted, and then immediately cooled to 0°. The reaction mixtures were analyzed on a F & M Model 5750 gas chromatograph using a 8 ft × $^1/_8$ in. column packed with 15% E600 on Chromosorb W. The peak areas of the epimeric alcohols and the internal standard were used to determine the amount of epimeric alcohols remaining in the sample. The relative reactivity ratios were calculated from the initial quantities and amounts remaining of each epimer using the equation

$$\frac{k_{\text{threo}}}{k_{\text{erythro}}} = \frac{\log (\text{threo})_i/(\text{threo})_f}{\log (\text{erythro})_i/(\text{erythro})_f}$$

where the subscripts i and f refer to the initial and final amounts, respectively.

Control Experiments.—When heated for several hours at 125° in the absence of *tert*-butyl peroxide, the isomeric halohydrins and hydroxy sulfides did not yield 2-butanone as a reaction product. All of the compounds did show some degree of thermal instability but decomposed at considerably slower rates than the *tert*-butyl peroxide induced reactions yielding 2-butanone. The thermal decomposition products were not identified.

Registry No.—IV, 10325-40-3; V, 10325-41-4; VIII, 19773-41-2; IX, 19773-40-1; X, 27022-36-2; XI, 27022-37-3.

---

[5] P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Amer. Chem. Soc.*, **85**, 2849 (1963).

[6] All boiling points are uncorrected. Elemental analyses performed by Wiler and Straus, Oxford, England.

[7] G. H. Coleman and F. J. Johnstone, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 158.

[8] E. R. Alexander and D. C. Dittmer, *J. Amer. Chem. Soc.*, **73**, 1665 (1951).

[9] D. J. Pasto and C. C. Cumbo, *J. Org. Chem.*, **30**, 1271 (1965).

[10] C. E. Wilson and H. J. Lucas, *J. Amer. Chem. Soc.*, **58**, 2399 (1936).

[11] J. K. Kochi and D. M. Singleton, *ibid.*, **90**, 1582 (1968).

On the Reality of Solvent Effects in the Decomposition of *tert*-Butyl Peroxide[1]

CHEVES WALLING* AND DOUGLAS BRISTOL

Department of Chemistry, University of Utah,
Salt Lake City, Utah 84112

Received August 17, 1970

Although the rate of decomposition of *tert*-butyl peroxide was originally described as essentially the same in the gas phase and a variety of solvents,[2] appreciable variations have subsequently been reported. The decomposition rate of the pure liquid peroxide is increased severalfold by an induced decomposition[3]

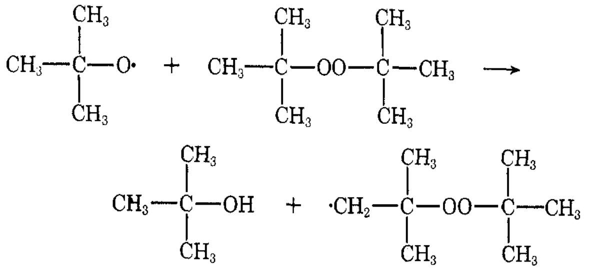
---

[1] Partial support of the work by a grant from the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

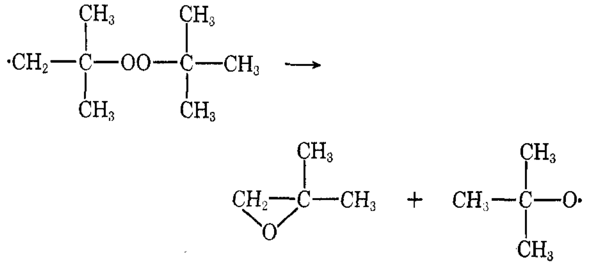
[2] J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, **70**, 1336 (1948).

[3] E. R. Bell, F. F. Rust, and W. E. Vaughan, *ibid.*, **72**, 337 (1950).

via steps 1 and 2, and induced chains have also been observed in the presence of HCl[4] and SF_6[5] in the gas phase and in the liquid phase in the presence of primary and secondary alcohols[6] or amines[7] and, *via* a more rapid electron transfer process, in the presence of alkoxide anions.[8] On the other hand, a reduction in decomposition rate is observed in viscous solvents,[9] due apparently to cage recombination of *tert*-butoxy radicals, and a similar viscosity dependence of quantum yield has been reported for the photochemical decomposition.[10]



$$(CH_3)_3CO\cdot + (CH_3)_3COOC(CH_3)_3 \longrightarrow (CH_3)_3COH + \cdot CH_2C(CH_3)_2OOC(CH_3)_3 \quad (1)$$



$$\cdot CH_2C(CH_3)_2OOC(CH_3)_3 \longrightarrow \underset{\diagdown O \diagup}{CH_2-\overset{CH_3}{C}-CH_3} + (CH_3)_3CO\cdot \quad (2)$$

Recently Huyser and Van Scoy[11] have reported a further effect of solvent polarity on the decomposition rate, and more particularly on heats and entropies of activation. Although their results lie in the order expected from data on solvent effects on the reactions of *tert*-butoxy radicals,[12] the magnitude of the effect is surprisingly large. Thus, for the extreme cases, cyclohexane and acetonitrile, $\Delta H^{\ddagger}$ is reported as 40.8 and 31.0 kcal/mol, respectively, and $\Delta S^{\ddagger}$ as +21.1 and −1.54 eu. Since their data were obtained at relatively high peroxide concentrations (5:1 solvent:peroxide mole ratios) and since those solvents in which decomposition was fast in general lacked reactive C–H bonds which could interrupt the chain sequence (1–2), it seemed to us that induced decomposition might account for their results, or, alternatively, they might be an artifact arising from the limited temperature range (15°) over which measurements were made.[13]

We have investigated the products of *tert*-butyl peroxide decomposition in several of Huyser's solvents at 125° and his concentrations, using isobutylene oxide yields as a measure of induced decomposition. In acetonitrile, the fastest solvent, it amounts to about 5% over the first half-life and is independent of conversion indicating that larger amounts are not being formed but then consumed in further reactions. Qualitatively similar yields are obtained in nitrobenzene and benzene, but they are lower in cyclohexane and negligible in cyclohexene, a good trap for both *tert*-butoxy and methyl radicals. At 100:1 acetonitrile:peroxide ratios, the isobutylene oxide yield is also negligible, although the decomposition rate is unchanged (see below). Accordingly we conclude that induced decomposition does not make a significant contribution to Huyser's rates.

Huyser's data indicate an isokinetic temperature for all his solvents at 164°, so that rates should diverge at lower temperatures. We have measured decomposition rates in acetonitrile and cyclohexene at 125 and 95° and cyclohexane at 95° (Table I). At the lower temperature the ratio is considerably lower (3.84) than predicted by Huyser's parameters (7.16). Figure 1 is an Arrhenius plot combining both sets of data. Also included are the only other set of low-temperature data available: Offenbach and Tobolsky's measurements employing styrene polymerization as a measure of decomposition rate.[14] Table II lists heats and entropies of activation calculated from the data shown in Figure 1. For styrene it was assumed that the decomposition rate at 120–135° was the same as reported by Huyser and Van Scoy in benzene, and also included are the results of Batt and Benson[15] for the reaction in the gas phase over an extended but higher temperature range.

TABLE I

RATE CONSTANTS FOR DECOMPOSITION OF *tert*-BUTYL PEROXIDE[a]

Solvent, mol ratio	Temp, °C	k, sec^{-1} × 10^7
Acetonitrile, 5:1	125	377 ± 9
Acetonitrile, 101:1	125	389 ± 20
Acetonitrile, 5:1	125	347 ± 4[b]
Cyclohexene, 5:1	125	149 ± 3
Cyclohexene, 5:1	125	138 ± 2[b]
Acetonitrile, 104:1	95	9.53 ± 0.10
Acetonitrile, 104:1	95	9.24 ± 0.18[c]
Cyclohexane, 98:1	95	2.48 ± 0.11

[a] All by disappearance of peroxide unless indicated. Experimental errors are standard deviations. [b] Data of Huyser and Van Scoy. [c] By appearance of products.

TABLE II

ACTIVATION PARAMETERS IN DECOMPOSITION OF *tert*-BUTYL PEROXIDE[a]

Solvent	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
Acetonitrile	34.2	6.5
Styrene[b]	34.8	6.7
Cyclohexane	38.4	15.2
Gas phase[c]	37.4	12.9

[a] Calculated by least square fit of data, Figure 1. [b] Styrene and benzene points combined. For styrene alone,[14] $\Delta H^{\ddagger}$ = 34.0 kcal/mol, $\Delta S^{\ddagger}$ = 4.6 eu. [c] Reference 15.

---

[4] M. Flowers, L. Batt, and S. W. Benson, *J. Chem. Phys.*, **37**, 2662 (1962).

[5] L. Batt and F. R. Cruickshank, *J. Phys. Chem.*, **70**, 723 (1966).

[6] E. S. Huyser and C. J. Bredeweg, *J. Amer. Chem. Soc.*, **86**, 2401 (1964).

[7] E. S. Hyyser, C. J. Bredeweg, and R. M. Van Scoy, *ibid.*, 4148 (1964).

[8] W. V. Sherman, *ibid.*, **90**, 6773 (1968).

[9] C. Walling and H. P. Waits, *J. Phys. Chem.*, **71**, 2361 (1967).

[10] H. Kiefer and T. G. Traylor, *J. Amer. Chem. Soc.*, **89**, 6667 (1967).

[11] E. S. Huyser and R. M. Van Scoy, *J. Org. Chem.*, **33**, 3524 (1968).

[12] C. Walling and P. Wagner, *J. Amer. Chem. Soc.*, **86**, 3363 (1964).

[13] Although Huyser and Van Scoy assign experimental uncertainties to their parameters based on error analysis, these do not, of course, exclude the possibility of systematic errors of unforeseen nature. Over a 15° temperature range, a 5% uncertainty in k's (which is modest) corresponds to a 1.5 kcal uncertainty in $\Delta H^{\ddagger}$.

[14] J. A. Offenbach and A. V. Tobolsky, *J. Amer. Chem. Soc.*, **79**, 278 (1957).

[15] L. Batt and S. W. Benson, *J. Chem. Phys.*, **36**, 895 (1962).

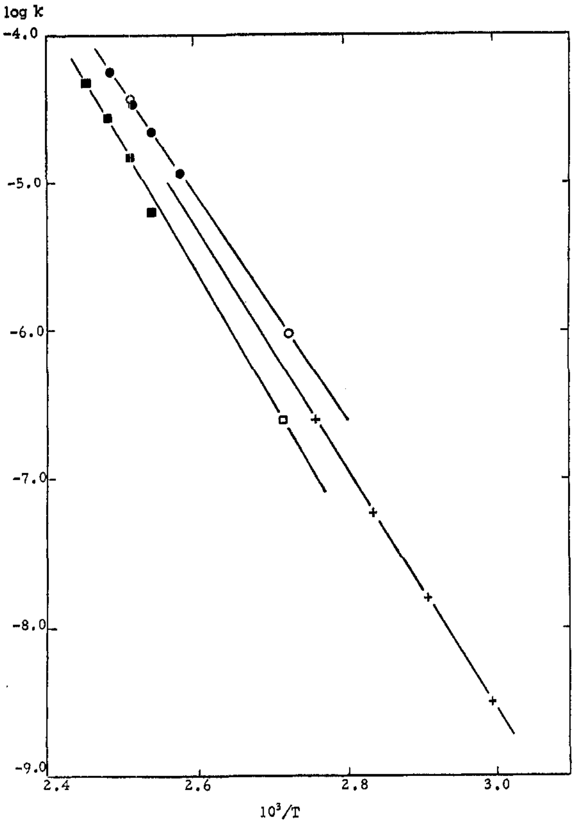


Figure 1.—Solvent effects on temperature dependence of *tert*-butyl peroxide decomposition: circles, acetonitrile; squares, cyclohexane; crosses, styrene; solid symbols, Huyser and Van Scoy; open symbols, this paper.

From Table II we conclude that, while the rate and activation parameters for the decomposition of *tert*-butyl peroxide do vary measurably with solvent, the magnitude of the effect is considerably less than reported by Huyser and Van Scoy. We also believe that our results point up the importance of determining activation parameters from data gathered over as wide a temperature range as possible. To place the matter in perspective, variations in rate of decomposition of *tert*-butyl peroixde with solvent and attributable to variations in reactant and transition-state solvation are comparable to or smaller than those previously observed with simple diacyl peroxides and peresters which decompose by single-bond scission and far smaller than the effects observed in those peroxides which decompose rapidly by concerted multibond scission.[16]

Experimental Section

Materials.—Peroxide and solvents were commercial materials, purified as necessary by conventional means and checked by gas-liquid chromatography (glc).

Decompositions.—Were carried out in sealed, degassed tubes in suitable thermostats, and products and decomposition rates were determined by glc analysis, using suitable internal standards added after reaction. Reaction rates were determined by monitoring either undercomposed peroxide or the appearance of products (*tert*-butyl alcohol plus acetone). Data on columns and conditions found effective for the different systems investigated appear in Table III.

Analysis of Data.—Rate constants were calculated from points from individual runs (usually 9), distributed in time over approximately 0.5–2 half-lives. Runs in both solvents at 95% were run concurrently to compensate for any drift in thermostat temperature over the 1–2 weeks required to achieve adequate reaction.

TABLE III

GAS CHROMATOGRAPHIC DATA

Analytical column[a]	Column temp, °C[b]	Compounds analyzed[c]	Solvent
12 ft, 15% diisodecylphthalate	40	Acetone, isobutylene oxide, *tert*-butyl peroxide, 2-pentanone	Acetonitrile, cyclohexene, cyclohexane, *tert*-butyl alcohol, benzene, nitrobenzene
12 ft, 20% DEGS in tandem with 15 ft, 20% FFAP	68	*tert*-Butyl peroxide, acetone, *tert*-butyl alcohol, benzene[d]	Acetonitrile
12 ft, 10% silicone gum rubber UCC-W982	40	*tert*-Butyl alcohol, methylcyclohexane,[d] *tert*-butyl peroxide	Cyclohexane

[a] Stationary phase, 80–100 mesh VarAport 30. [b] Injector temp, 70–80°. [c] In order of elution. [d] Internal standard.

Registry No.—*tert*-Butyl peroxide, 110-05-4.

---

[16] For a recent discussion of such systems, *cf.* C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappiaonnov, *J. Amer. Chem. Soc.*, **92**, 4927 (1970).

Diacetylation of Amines

R. P. MARIELLA* AND K. H. BROWN[1]

Department of Chemistry, Loyola University, Chicago, Illinois 60626

Received June 18, 1970

Several representative primary amines were acetylated under reflux conditions Table I shows the results of the treatment of these amines with boiling acetic anhydride. Those primary amines of the type RCH_2NH_2 gave reasonably good yields of only *N*,*N*-diacetylamines, $RCH_2N(COCH_3)_2$. Primary amines of the type $RR'CHNH_2$ gave *N*-monoacetylamines, $RR'CHNHCOCH_3$, and *N*,*N*-diacetylamines depending on the nature of R and R′. $RR'R''CNH_2$ gave only *N*-monoacetylamine. Mono- or diacetylation is clearly a function of the steric requirements about the amino group. The reaction provides a useful route for obtaining *N*,*N*-diacetylamines in reasonably good yields, as shown in Table I.

The infrared spectra of the *N*-monoacetylamines show bands at 3225–3275 cm^{-1} due to the N–H stretch of amides of the type CH_3CONHR. In all compounds prepared, whether monoacetylamine or diacetylamine, the symmetrical N–H stretch of the methyl group in the acetyl function shows absorption at 1366–1374 cm^{-1}. The carbonyl group of the monoacetylamines show a strong band at *ca.* 1640 cm^{-1}. The carbonyl band of the diacetylamines show up at 1692 cm^{-1}. The difference in the frequency of absorption of the carbonyl group for monoacetylamines and diacetylamines was

---

[1] Taken from the Ph.D. Dissertation of K. H. Brown, Loyola University, 1970.