

Electron Spin Resonance Measurements of the Termination Rate Constants for t-Butyl Radicals in Solution

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The rate constants, $2k_t$, for the mutual termination of t-butyl radicals in liquid isobutane and cyclopentane have been measured in the temperature range 170–330 K, by kinetic e.s.r. spectrometry. The results are in excellent agreement with values of $2k_t$ reported recently for termination in a series of n-alkanes. It is concluded that the termination reaction is completely diffusion-controlled in both solvents. The value of $2k_t$ ($11 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) at 298 K is in good agreement with that derived from recent gas phase measurements ($2k_t = 9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) at the same temperature.

THERE has been considerable recent interest in the rate constants of the termination reactions for alkyl radicals in both gas and liquid phases. Previously, the generally accepted values¹ of the rate constants, $2k_c$, for the recombination of the larger alkyl radicals (ethyl, isopropyl, and t-butyl) were those measured by the rotating sector technique, which gave values in the range 10^9 – $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. However, Hiatt and Benson² have obtained much lower values of $2k_c$ for these radicals, and in particular for the t-butyl radical ($2k_c = 5 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 373 K). Konar, Marshall, and Purnell³ also report a low value for the recombination of the t-butyl radical ($2k_c = 3 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). In contrast, measurements^{4–9} by e.s.r. spectrometry have given values of the overall termination rate constant ($2k_t = 10^9$ – $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) for the t-butyl radical in the liquid phase that are very similar to those from the original gas phase results ($2k_t = 2k_c + 2k_a$, where $2k_a$ is the rate constant for the disproportionation reaction and in the gas phase $k_a/k_c \approx 3$; $2k_t$ is defined by $-d[R\cdot]/dt = 2k_t[R\cdot]^2$).

Recently, a direct measurement of the rate constants for the termination reactions of several alkyl radicals in the gas phase has been made in our laboratories by using a molecular modulation spectrometer.^{10,11} In particular,¹¹ a value of $2k_t$ of $9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ has been

to attempt a further measurement by e.s.r. in the liquid phase to permit a direct comparison with our gas phase measurements.

Since our preliminary note⁹ on this work, Schuh and Fischer¹² have reported extensive measurements of the termination rate constants for the t-butyl radical in a range of alkane solvents. The radicals were produced by irradiation of solutions of 2,2,4,4-tetramethylpentan-3-one (di-t-butyl ketone; DTBK) in various alkanes over the temperature range 290–370 K. Our results, which have been obtained at lower temperatures and by use of a different method to prepare the radicals, are in good agreement with those of Schuh and Fischer.

We have made measurements of $2k_t$ over the temperature range 150–260 K, using the photolysis of di-t-butyl peroxide (DTBP) in isobutane as the source of t-butyl radicals. For comparison with the results¹² for termination in alkanes at higher temperature we have also prepared the radicals by the photolysis of DTBK in cyclopentane over the intermediate temperature range 200–350 K.

Although the photolysis of 2,2'-dimethyl-2,2'-azopropane (DAP) is a satisfactory source of t-butyl radicals in the gas phase,¹¹ we have found that it is not suitable for kinetic measurements in the liquid phase because of the formation of the thermally unstable *cis*-isomer of the azo-compound.

Termination rate constants for t-butyl radicals in the liquid phase

Initiator; solvent	T/K	$\frac{2k_t \times 10^{-9}}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$	Ref.
DAP; benzene	298	1.5	4
DAP; cyclohexane	298	4.4	4
DTBP sat. with Bu ^t H	298	8.1	5
DTBK; benzene	282	5.7	7
DAP; toluene	218	9.8	9

obtained for the overall termination of the t-butyl radical at 300 K. In view of this result and the range of values observed in the liquid phase (Table) it seemed opportune

¹ E. L. Metcalfe, *J. Chem. Soc.*, 1960, 3560.

² R. Hiatt and S. W. Benson, *Internat. J. Chem. Kinetics*, 1973, **5**, 385.

³ R. S. Konar, R. M. Marshall, and J. H. Purnell, *Internat. J. Chem. Kinetics*, 1973, **5**, 1007.

⁴ S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, 1969, **91**, 986.

⁵ G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 491.

⁶ D. Griller and K. U. Ingold, *Internat. J. Chem. Kinetics*, 1974, **6**, 453.

EXPERIMENTAL

The experimental method entails the combination of rapid recording e.s.r. spectrometry and intermittent photolysis using a rotating sector. The t-butyl radicals are formed by photolysis of a suitable chemical precursor and the change in their concentration with time is measured by following the corresponding change in intensity of the e.s.r. spectrum. The output from the spectrometer is stored in a digital signal averager to obtain sufficiently fast response, and the signal-to-noise ratio is enhanced by accumulating several thousand individual decay curves.

⁷ E. J. Hamilton and H. Fischer, *J. Phys. Chem.*, 1973, **77**, 722.

⁸ H. Schuh, E. J. Hamilton, H. Paul, and H. Fischer, *Helv. Chim. Acta*, 1974, **57**, 2011.

⁹ J. E. Bennett, J. A. Eyre, C. P. Rimmer, and R. Summers, *Chem. Phys. Letters*, 1974, **26**, 69.

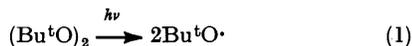
¹⁰ D. A. Parkes, D. M. Paul, and C. P. Quinn, *J.C.S. Faraday I*, 1976, 1935.

¹¹ D. A. Parkes and C. P. Quinn, *J.C.S. Faraday I*, 1976, 1952.

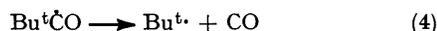
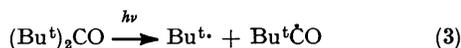
¹² H. Schuh and H. Fischer, *Internat. J. Chem. Kinetics*, 1976, **8**, 341.

Radical Preparation.—The t-butyl radicals were prepared by photolysis of a suitable precursor in a solvent which was thoroughly degassed by repeated freeze–thaw cycles under vacuum. For method (b) or (c) the free space in the e.s.r. sample tube was filled with pure nitrogen (BOGC 'white spot') to suppress evolution of gas (N_2 or CO) during photolysis.

Three chemical systems were used: (a) di-t-butyl peroxide (5% v/v) in isobutane [equations (1) and (2)];



(b) di-t-butyl ketone (1–5% v/v) in cyclopentane [equations (3) and (4)*]; and (c) 2,2'-dimethyl-2,2'-azopropane (5%



v/v) in cyclohexane, benzene, or toluene [equation (5)].



Apparatus.—The radiation source was a 200 W high-pressure mercury lamp (Mazda HBO 200). The light beam was focused in the plane of a rotating sector by a fused silica lens and then refocused onto the entrance grid of the e.s.r. cavity by a second lens. Care was taken to ensure that the illumination was uniform over the whole area of the grid. The rotating sector (diameter 150 mm) had two light and two dark periods per revolution, with a light : dark ratio of 2 : 1. A trigger pulse for the signal averager was obtained from a photoemissive/photosensitive pair of diodes placed almost diametrically opposite to the light beam. The sector was run at about 33 Hz, which corresponded to a cut-off time of 0.2–0.3 ms. (A typical first half-life for the radical decay was about 2 ms.)

The e.s.r. measurements were made with a Varian V-4502 EPR spectrometer. The sample temperature was controlled by a standard variable temperature accessory. The temperature of the gas flow was monitored with a thermocouple and the actual sample temperature was measured immediately after each experiment. The kinetic measurements were made by monitoring the amplitude of one of the central first-order hyperfine lines of the spectrum of the t-butyl radical (the second-order structure was only partially resolved). The absolute concentration of t-butyl radicals was determined by comparing the intensity of this central line with that of the spectrum of a standard sample of $\alpha\alpha'$ -diphenylpicrylhydrazyl.

An output was taken directly from the 100 kHz phase-sensitive detector of the spectrometer and passed through an impedance matching amplifier (gain $\times 10$) to a Data Laboratories Biomac 1000 Signal Averager. Up to 16 400 separate decay curves were accumulated for each run to obtain a reasonable signal-to-noise ratio.

For second-order kinetics the radical decay curve has a long tail and the true baseline, corresponding to zero concentration, cannot be obtained unless the dark period is

* Above 260 K the decarbonylation reaction (4) is fast, and reactions involving acyl radicals can be neglected.⁸ However, at lower temperatures the effects of both the decarbonylation and the cross-termination reactions of acyl radicals must be included in the overall kinetics of the t-butyl radicals.

very long in comparison with the initial part of the decay curve. To overcome this problem use was made of the facility in the Biomac Signal Averager, which permits the memory store to be split into four separate channels of 256 points each. A set of decay curves was accumulated in the first channel and then without photolysis an equal number of scans was accumulated in the second channel to obtain the baseline. These two runs were repeated and stored in the third and fourth channels, respectively. The four channels were read out separately to a chart recorder. Coincidence of the two decay curves (channels 1 and 3) and the two baselines (channels 2 and 4) apart from random noise showed that no drifts had occurred in the spectrometer. If there was a significant shift in either pair of curves the results from that set of measurements were discarded.

Materials.—The 2,2'-dimethyl-2,2'-azopropane was prepared by the method given by Stowell,¹³ and its purity by

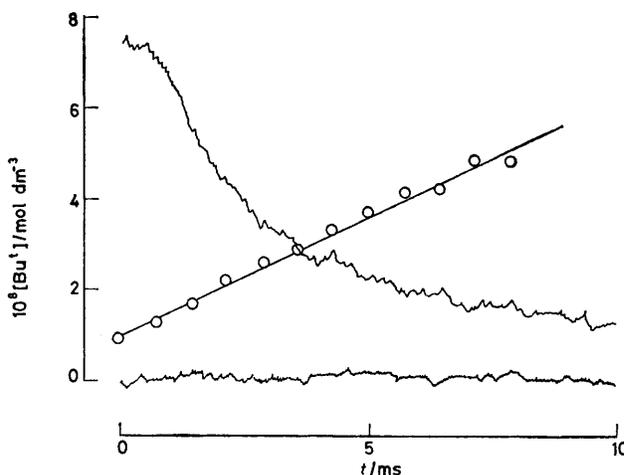


FIGURE 1 Decay of t-butyl radical at 238 K and corresponding second-order plot $[Bu^t]_0/[Bu^t]$

g.l.c. analysis was >98%. Di-t-butyl peroxide was obtained from Koch–Light and was purified by fractional distillation. Di-t-butyl ketone was Fluka purum grade and was used without further purification.

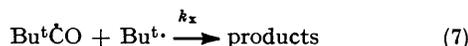
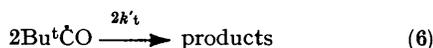
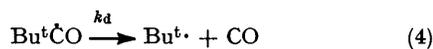
RESULTS

Di-t-butyl Peroxide in Isobutane.—Good second-order plots were obtained for the decays of the t-butyl radical over the temperature range 170–260 K. A typical decay curve and the corresponding second-order plot are shown in Figure 1. The Arrhenius plot for the termination rate constant, $2k_t$, is given in Figure 2. The activation energy, E_t , is 4.3 kJ mol⁻¹.

Di-t-butyl Ketone.—A series of measurements were made using di-t-butyl ketone in cyclopentane to span the temperature range between our results for termination in isobutane and those of Schuh and Fischer¹² for termination in normal alkanes. Second-order decays were obtained in cyclopentane over the temperature range 200–300 K. However, at the lower temperatures the decay kinetics are affected by the participation of the acyl radicals $Bu^t\dot{C}O$, because the rate of the decarbonylation reaction (4) is very

¹³ J. C. Stowell, *J. Org. Chem.*, 1967, **32**, 2360.

temperature-dependent. The rate constants for the termination reaction (6) and decarbonylation of the acyl radical have been obtained in methylcyclopentane.⁸



With the assumption that $k_x = 2(k'_t k_t)^{1/2}$, we have used these values to obtain computer simulations of the decays of t-butyl and acyl radicals under our experimental conditions. The concentration of acyl radicals is negligible above 215 K, and the effect on the decay rate of t-butyl radicals is only significant for temperatures below 210 K. The corrected values are shown in the Arrhenius plot in Figure 2. The activation energy, E_t , is identical with that observed in isobutane (4.3 kJ mol^{-1}).

2,2'-Dimethyl-2,2'-azopropane.—The results showed that this azo-compound (DAP) was not a satisfactory source of t-butyl radicals for kinetic measurements in the liquid phase. Accurate second-order decays were not observed at any temperature in the range 270–340 K. The departure from second-order behaviour was most marked at the lower temperatures where the kinetics were close to the first order (Figure 3). This behaviour is attributed to the formation of the *cis*-isomer of DAP during photolysis.⁹

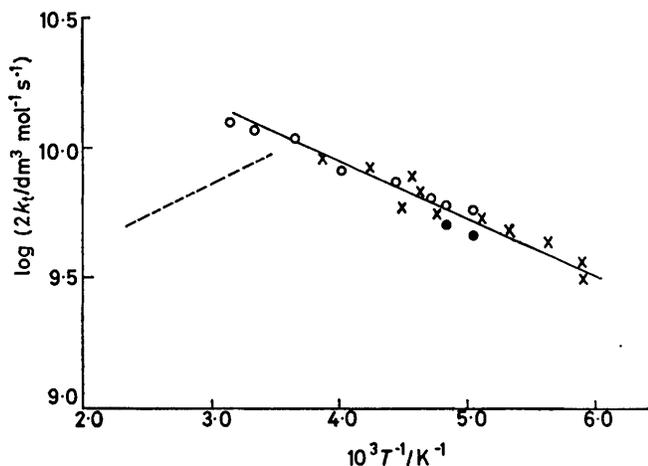
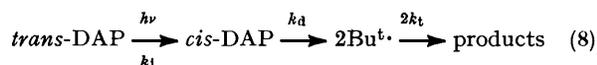


FIGURE 2 Arrhenius plots for termination of t-butyl radical: (○) in cyclopentane [(●) corrected for reactions of acyl radical]; (×) in isobutane; (---) gas phase results from ref. 11

The *cis*-isomer is about 80 kJ mol^{-1} less stable to dissociation than the normal *trans*-isomer, and consequently decomposes rapidly above 270 K. Thus the overall reaction is (8). During photolysis a steady state is established



[equation (9)], and on cessation of photolysis equation (10)

$$2k_1[\text{trans-DAP}] = 2k_d[\text{cis-DAP}]_{\text{ss}} = 2k_t[\text{Bu}^t\cdot]_{\text{ss}}^2 \quad (9)$$

$$-d[\text{Bu}^t\cdot]/dt = 2k_t[\text{Bu}^t\cdot]^2 - 2k_d[\text{cis-DAP}] \quad (10)$$

applies. Thus the observed decay of t-butyl radicals is not

second-order, and will depend on the value of $2k_d$ and the amount of *cis*-isomer formed during photolysis. A computer simulation based on equation (10), with $k_d = 5 \times 10^9$

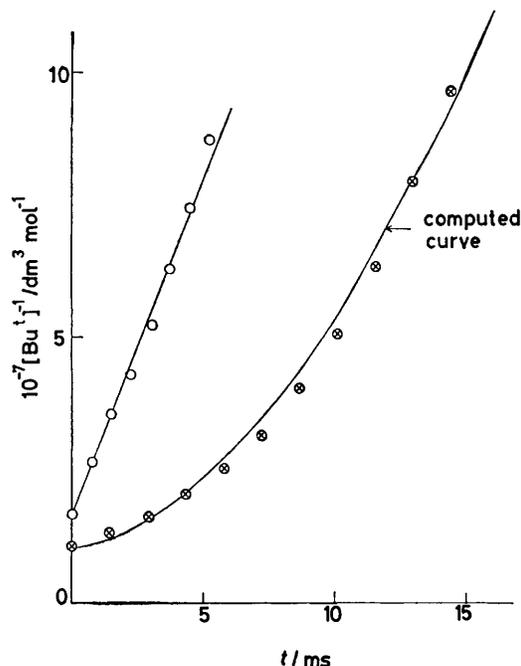


FIGURE 3 Second-order plots for decay of t-butyl radical: (○) DTBP-isobutane at 250 K; (●) = DAP-cyclohexane at 330 K

s^{-1} , $2k_t = 1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and $[\text{cis-DAP}]_{\text{ss}} = [\text{Bu}^t\cdot]_{\text{ss}} = 10^{-7} \text{ mol dm}^{-3}$, is compared in Figure 3 with the decay observed at 330 K in cyclohexane. A similar analysis of the decays at other temperatures showed that $2k_t$ lay in the range $1.0\text{--}1.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and that there was no difference between the values of the termination rate constants in cyclohexane or benzene.

DISCUSSION

Our results confirm that the rate constant for the overall termination of t-butyl radicals in the liquid phase is very close to $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K. This value is in good agreement with that ($8.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) obtained by Watts and Ingold⁵ for a saturated solution of isobutane in di-t-butyl peroxide. Griller and Ingold⁶ have shown that the ratio of the termination rate constants for t-butyl and ethyl radicals is close to 1:1, which again leads to a value for t-butyl close to $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. However, the present values are significantly higher than the values reported by Weiner and Hammond⁴ for termination in benzene and cyclohexane (1.5×10^9 and $4.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively). Our work has shown that these values are in error because 2,2'-dimethyl-2,2'-azopropane is not a satisfactory source of t-butyl radicals for kinetic measurements in the liquid phase. A correct analysis of the results leads to values of $2k_t$ close to $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in both benzene and cyclohexane at 298 K. Furthermore, the rate constants exhibit the same temperature dependence over the range 290–340 K.

Recently Schuh and Fischer¹² have carried out a detailed study of the termination rate constants for the t-butyl radical in a range of n-alkanes over the temperature range 290–360 K. At 298 K their values for $2k_t$ are also very close to $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, but they find that the activation energy varies significantly with solvent. The activation energies are, in fact, very close to the corresponding temperature coefficients, C , of viscosity as given by Andrade's theory [equation (11)].

$$\eta = A \exp C/T \quad (11)$$

Consequently they conclude that the recombination of t-butyl radicals is diffusion-controlled in the liquid phase.

The activation energies (4.3 kJ mol^{-1}) obtained from our measurements in isobutane and cyclopentane are smaller than those observed in the alkanes. These results are in accord with the smaller dependence of the viscosities of these solvents on temperature (the temperature coefficients, C , for isobutane and cyclopentane are 6.9 and 7.5 kJ mol^{-1} , respectively).

In view of the similarity of the two sets of results we follow the treatment given by Schuh and Fischer. For a diffusion-controlled reaction the overall rate constant can be expressed in terms of the Smoluchowski equation (12), where σ is the statistical factor which accounts for

$$2k_t^D = 8\pi\sigma D\rho N/1000 \quad (12)$$

the fact that only radical pairs which are in a singlet electronic state will lead to reaction; D is the diffusion constant; and ρ is the reaction distance. The diffusion constant D can be approximated by the Stokes–Einstein relationship (13), where η is the absolute viscosity of the

$$D = kT/6\pi r\eta \quad (13)$$

solvent and r is the diffusion radius of the radical. With the assumptions that $\rho = 2r$ and $\sigma = \frac{1}{4}$, a combination of equations (12) and (13) leads to equation (14).

$$2k_t^D = RT/1500\eta \quad (14)$$

Plots of the experimental rate constants against T/η are shown in Figure 4. The experimental values of $2k_t$ show a reasonably linear dependence on T/η , but are considerably higher than the values predicted by equation (14).

A number of semiempirical modifications have been made to the Stokes–Einstein equation to account for the observed rates of mutual and self-diffusion in liquids. In particular Schuh and Fischer have used the theory of microfriction proposed by Spornol and Wirtz.¹⁴ In this theory the diffusion coefficient is given by equation (15), where the microfriction factor, f , is introduced to

$$D = kT/6\pi r\eta f \quad (15)$$

take account of the fact that the radius, r_r , of the solute molecule is comparable with the radius, r_s , of the solvent molecule. The factor, f , is given by equation (16),

$$f = (0.4 + r_r/r_s)(0.36 + 0.16T_s - 0.1T_r) \quad (16)$$

where r_r and r_s are calculated from the molar volumes of the solute and solvent at temperature T , and T_r and T_s are reduced temperatures calculated from the melting and boiling points, T_M and T_B , of the solute and solvent [equation (17)].

$$T_r = \left(\frac{T - T_M}{T_B - T_M} \right)_{\text{solute}} \quad \text{and} \quad T_s = \left(\frac{T - T_M}{T_B - T_M} \right)_{\text{solvent}} \quad (17)$$

When the microfriction factor is calculated it is assumed that the physical properties of the t-butyl radical are similar to those of isobutane. Thus when

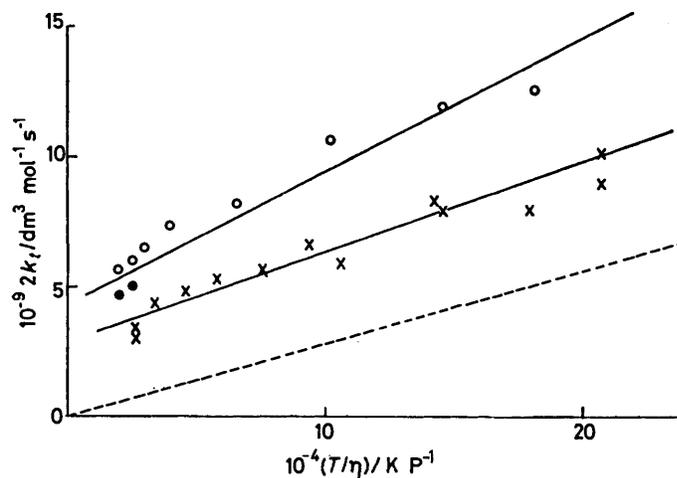


FIGURE 4 Plots of $2k_t$ against T/η for t-butyl radical: (○) in cyclopentane [(●) corrected for reactions of acyl radical]; (×) in isobutane; (---) line calculated from equation (14)

isobutane is used as the solvent, equation (16) reduces to equation (18). The physical data required in equations

$$f = 1.4(0.36 + 0.06T_s) \quad (18)$$

(14)–(18) were taken from the compilation by Gallant,¹⁵ with extrapolation of the values to lower temperatures where necessary. The plots of $T/\eta f$ are shown in Figure 5 together with the recent results obtained by Schuh and Fischer¹² for the termination of the t-butyl radical in a series of n-alkanes (C_7 , C_8 , C_{10} , C_{12} , C_{14} , and C_{16}).

Our values for $2k_t$ in isobutane are in reasonable agreement with those for the C_7 – C_{16} alkanes. The agreement is particularly satisfying in view of the fact that the two sets of results were obtained under different experimental conditions. Schuh and Fischer used di-t-butyl ketone as the source of t-butyl radicals and made their measurements of $2k_t$ over the temperature range 290–370 K; their steady-state concentrations of t-butyl radicals were about $10^{-6} \text{ mol dm}^{-3}$. In our experiments the t-butyl radicals were formed by abstraction from isobutane, and the measurements of $2k_t$ were made over the temperature range of 170–

¹⁴ A. Spornol and K. Wirtz, *Z. Naturforsch.*, 1953, **8a**, 522.

¹⁵ R. W. Gallant, 'Physical Properties of Hydrocarbons,' Gulf Publishing Co., Houston, 1968.

260 K; the steady-state concentrations of t-butyl radicals were about 10^{-7} mol dm $^{-3}$, a factor of 10 less than those used by Schuh and Fischer.

Our results for $2k_t$ in cyclopentane (di-t-butyl ketone as the source of t-butyl radicals) do not fit as satisfactorily, and the results of Schuh *et al.*⁸ for methylcyclopentane also deviate in the same direction (Figure 5). It appears that the diffusion constants in these cyclic alkanes are higher than those predicted from the

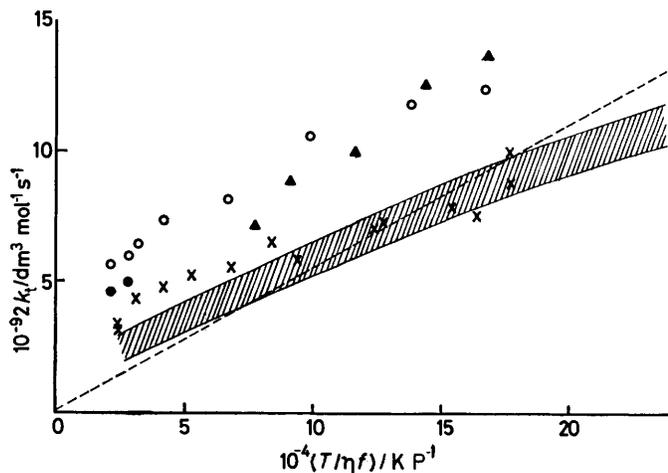


FIGURE 5 Plots of $2k_t$ against $T/\eta f$ for t-butyl radical: (○) in cyclopentane [(●) corrected for reactions of acyl radicals]; (×) in isobutane; (▲) in methylcyclopentane (ref. 8); (---) line calculated from equations (12) and (15); shaded area is the range of $2k_t$ in various alkanes (ref. 12).

bulk viscosity with the inclusion of the effect of microfriction.

The expression derived by Spornol and Wirtz¹⁴ for the microfriction factor, f , is an average obtained from experimental plots of f against r_t/r_s for a range of solutes and solvents. The values of f for isobutane (0.54–0.59) and cyclopentane (0.4–0.54), which we have calculated from this expression, are comparable. However in the actual plots given by Spornol and Wirtz the values for hexane and cyclohexane (as solvents) show the largest deviations from the mean and occur in opposite directions. Thus in the range of $r_t/r_s \approx 1$, which is applicable to our results, the value of f (cyclohexane) is about $0.6f$ (hexane). Consequently use of the

average relationship may overestimate the values of f for the cycloalkanes relative to those for the alkanes and thus under estimate the values of $T/\eta f$ for the cycloalkanes by a factor of about 1.7. A correction by this factor to the points plotted in Figure 5 would bring the values for cyclopentane and methylcyclopentane into reasonable agreement with those for the alkanes.

The overall success of the treatment indicates that the termination rate constants for the t-butyl radical in these solvents are completely diffusion-controlled. Further, there are no strong interactions between the radical and the solvent, as suggested by Weiner and Hammond.⁴ Also the good agreement between the values obtained by the different methods of initiation and in different solvents is an indication that the observed rate constants are not affected significantly by geminate recombination of the radicals in a solvent cage.²

The recent gas-phase measurements by Parkes and Quinn¹¹ using molecular modulation spectroscopy give a value for $2k_t$ of 9×10^9 dm 3 mol $^{-1}$ s $^{-1}$ at 300 K and show that there is a slight negative temperature dependence. Very recently Choo and his co-workers¹⁶ have obtained a value of 6×10^8 dm 3 mol $^{-1}$ s $^{-1}$ at 700 K for the recombination rate constant $2k_c$. The corresponding value of $2k_t$ is about 2×10^9 dm 3 mol $^{-1}$ s $^{-1}$, which is in good accord with the negative temperature dependence observed by Parkes and Quinn.¹¹

As pointed out by several authors^{6,11,16} these recent results cast serious doubt on the validity of the currently accepted thermochemistry for alkyl radicals, on which the anomalously low values of $2k_c$ in the gas phase have been based.^{2,3}

There is good agreement between the rate constants measured in the liquid phase and the recent gas phase values. However the opposite temperature dependence in the two phases indicates that the transition states are different. In the liquid phase diffusion into a cage is the rate controlling process and obscures the effects of structure in the gas phase intermediate.

We thank Mr. F. R. Heather for preparing the dimethyl azopropane.

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¹⁶ K. Y. Choo, P. C. Beadle, L. W. Piszkiwicz, and D. M. Golden, *Internat. J. Chem. Kinetics*, 1976, 8, 45.