200. The Kinetics of the Bimolecular Sel-Reaction of *t*-Butyl Radicals in Solution. I. Termination Rates[1])

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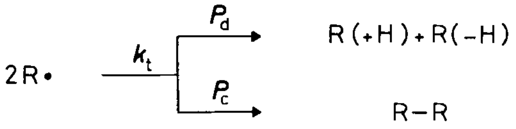
Summary

Termination rate constants $2K_t$ for the self-reaction of *t*-butyl radicals in twelve different solvents are determined as a function of temperature by kinetic electron spin resonance. In the entire range measured, $7 \cdot 10^7 < 2k_t < 2 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1}, they are well described by the *von Smoluchowski* equation for diffusion controlled reactions, using a spin statistical factor, a temperature and solvent independent, isotropic reaction diameter, and diffusion coefficients for *t*-butyl estimated following empirical or semiempirical prescriptions. Methods for the prediction of diffusion coefficients are critically discussed, and rules for the estimation of termination rate constants of steric unhindered alkyl radicals are suggested.

1. Introduction. - If two identical free radicals R· such as *t*-butyl meet in solution, they may react with each other, *i.e.* self-terminate with the overall rate constant k_t to form products. For alkyl radicals with β-hydrogen atoms two product channels are available: a) disproportionation to an alkane R(+H) and an alkene R(−H) by transfer of a β-hydrogen atom (1); b) combination to the dimer alkane R-R (2) [1-3].



$$2R\bullet \xrightarrow{k_t} \begin{cases} \xrightarrow{P_d} R(+H) + R(-H) & (1) \\ \xrightarrow{P_c} R-R & (2) \end{cases}$$

The percentages undergoing disproportionation P_d or combination P_c are specific for the radical considered, and for most cases depend weakly on temperature and solvent. Several factors governing disproportionation *vs.* combination ratios P_d/P_c have been discussed, but so far no generally acceptable interpretation has been found [1].

Unless severe steric hindrance interferes, the termination rate constant k_t is of the order of magnitude expected for rate control by translational diffusion [1-9].

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[1]) Part of the Ph.D. Thesis of *H. Schuh*, Universität Zürich, 1978.

However, due to both theoretical and experimental difficulties, the extent of diffusion control, *i.e.* the average number of unreactive radical encounters, has been a matter of speculation [1] [3] [5b].

In this and a following paper [8] the temperature and solvent dependence of both the termination rate constant k_t and the product ratio P_d/P_c are studied in detail for one typical alkyl radical, namely *t*-butyl. Evidence is presented for complete control of k_t by translational diffusion and for anisotropic reorientation of paired radicals in the solvent cage as the factor determining the product ratio P_d/P_c. In particular, in this paper the pertinent literature on the termination kinetics of *t*-butyl and its generation *via* photolysis of di-*t*-butylketone is briefly surveyed in chapter 2. The determination of rate constants by kinetic electron spin resonance (ESR.) and by product analysis is described in chapter 3, together with other experimental details. The results (chapter 4) are interpreted in chapter 5 in terms of the conventional theory of diffusion controlled reactions. Several empirical and semiempirical procedures for the prediction of diffusion coefficients are used and critically compared. In a concluding section the treatment is extended to other radicals.

2. Termination kinetics of *t*-butyl radicals and photolysis of di-*t*-butylketone. -

Literature values for the self-termination rate constant k_t of *t*-butyl radicals in solution are compiled in *Table 1*. They are typical for alkyl radicals and may be characterized as follows: i) the rate constants lie in the range 10^9-10^{10} $dm^3 \cdot mol^{-1} \cdot s^{-1}$. This is close to the diffusion controlled limit [1-15]; ii) the experimental scatter is considerable, deviations of a factor 5.5 or 7 for nearly identical experimental conditions (*cf.* benzene or isobutane solutions, *Table 1*) suggest the data to be nothing more than good estimates of the order of magnitude [5b]; iii) the independence of the rate constants on temperature over a considerable range as stated by different authors for toluene [12] or isobutane [15] solutions, is incompatible with the expected viscosity dependence for a diffusion controlled reaction [1-3].

Obviously, if a discussion of the factors influencing the rate constants is intended to be more than mere speculation, accurate measurements of k_t over wide ranges of temperature and viscosity are needed. For this purpose, an efficient and well-understood source for generating *t*-butyl radicals is required, together with a reliable measuring technique.

Of the four photochemical systems suited for the generation of *t*-butyl radicals in solution *(Table 1)*, the photolysis of di-*t*-butylketone was chosen (for other techniques see [2] [6] [16]). This method was preferred, since the organotinhydride-alkylhalogenide system involves rather complex kinetics [9], azoisobutane is unsuitable as a photo-initator in time-resolved experiments [15], and finally, because formation of acetone and methyl radicals [17], or unexplained dependencies of the rate constants k_t on the initiator concentration [18], complicate the di-*t*-butylperoxide photolysis.

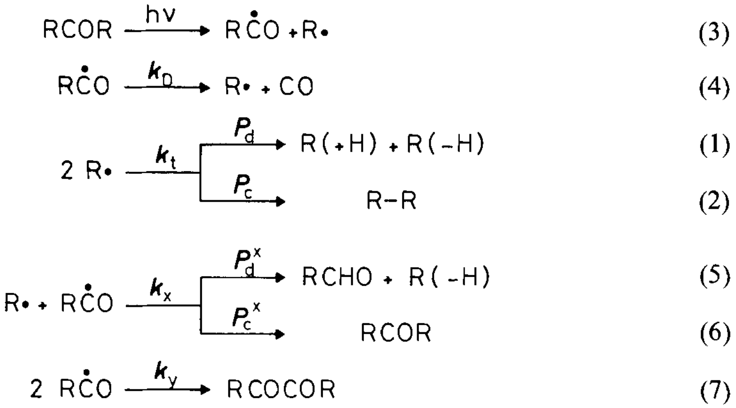
The photolysis of di-*t*-butylketone RCOR ($R=(CH_3)_3C$) in solution has been extensively investigated by several authors [14] [19-23] and may be summarized as follows: UV. excitation in the $n\pi^*$-transition band of RCOR leads, *via* α-cleavage,

Table 1. *Termination rate constants $2k_t$ of photochemically generated* t-*butyl radicals*

Initiator	Solvent	T [K]	$2k_t$ [$10^9 \cdot dm^3 \cdot mol^{-1}s^{-1}$]	References
AIB[a]	benzene	298	1.5	[10]
RCOR[b]	benzene	292	5.7	[13]
RCOR	benzene	298	8.2	[14]
AIB	toluene	218-330	9.8	[15]
ACHN/*t*BBr-RSnH[c]	cyclohexane	298	2.1	[9]
AIB	cyclohexane	298	4.4	[10]
RCOR	MCP[e]	298	10.2	[14]
ACHN/*t*BBr-RSnH	pentane	298	5.4	[9]
ACHN/*t*BBr-RSnH	tridecane	298	1.8	[9]
DBPO[d]	DBPO[f]	298	8.1[g]	[11]
DBPO	isobutane	250	11.1	[15]
DBPO	isobutane	188-262	1.6	[12]

[a] Azoisobutane. [b] Di-*t*-butylketone. [c] Azobiscyclohexyl nitrile/*t*-butylbromide and organotinhydrides. [d] Di-*t*-butylperoxide. [e] Methylcyclopentane. [f] Saturated with isobutane. [g] Revised by a factor of $\frac{1}{3}$ in later work [4b] [12].

predominantly from the triplet state [21], to the primary radicals pivaloyl $R\dot{C}O$ and *t*-butyl $R^{\cdot}$. The resulting products [19] [21-23], carbon monoxide CO, isobutane R(+H), isobutene R(−H), hexamethylethane R-R, pivalaldehyde RCHO, the diketone RCOCOR and back-formed ketone RCOR [21] [22], are compatible with the following reaction scheme:



Kinetic parameters obtained by measurements of $R\dot{C}O$ and $R^{\cdot}$ in methylcyclopentane [14] are in reasonable agreement with those derived from product yields in tetramethylsilane (TMS) [22]. The product yields are markedly temperature dependent since the decarbonylation reaction (4) of the pivaloyl radical is strongly activated. At elevated temperatures the lifetime of $R\dot{C}O$ is very short. For methylcyclopentane at 40 °C we determined $\tau = 4$ µs [14], which is in excellent accord [5a] with a value found independently by a different technique in benzene ($\tau = 3.9$ µs at 40 °C, [24]). Since for usual concentrations the radicals terminate nearly a hundred times slower (*cf.* chapter 3), the decarbonylation (4) efficiently suppresses reactions (5)-(7). Accordingly, negligible amounts of pivalaldehyde RCHO are found at room temperature [8] [22] [23], (for medium effects see [8]). Only below 0 °C ($\tau > 35$ µs) is a direct observation of the pivaloyl radical possible [14] [20]. The following side reactions (8-10), *i.e.* hydrogen abstraction (8) by *t*-butyl from the solvent SH, photoreactions (9) of the products RCOCOR [14] [20] or RCHO [21], and the addition (10) of the *t*-butyl radical to isobutene [8] [25] can be largely suppressed by the choice of inert solvents and by low conversion of the starting ketone,

$$R\bullet + SH \longrightarrow R(+H) + S\bullet \tag{8}$$

$$RCOCOR\ ;\ RCHO \xrightarrow{h\nu} \text{products} \tag{9}$$

$$R\bullet + R(-H) \longrightarrow R\text{-}\dot{R}(-H) \tag{10}$$

If these reactions (8-10) are unimportant and decarbonylation (4) is fast compared to the termination (1, 2, 5-7), the photolysis of di-*t*-butylketone above *ca.* 0°C provides a clean and efficient source for *t*-butyl radicals with a quantum yield of about 1.4 [19] [21].

3. Experimental. - 3.1. *Solvents and sample preparation.* Heptane, octane, decane, dodecane, tetradecane, hexadecane, acetonitrile, benzene, octamethylcyclotetrasiloxane (OMCTS), *t*-butylalcohol (*t*-ButOH), 3-methyl-3-pentanol (3MP) and a 1:2 molar mixture of *t*-butyl alcohol: pinacol (*t*-ButOH/Pin) were chosen as solvents because of accessible transport and thermodynamic properties and inertness to radical attack. Where UV. or GLC. analysis revealed impurities the solvents were purified by distillation over a *Widmer* or a spinning band column. Water-free pinacol was recrystallized first from hexane and then from pentane at 0 °C. No special attempts were made to avoid contact with atmospheric moisture during the recrystallization.

All solutions employed in the kinetic and viscosity measurements contained 3 Vol% (0.17 mol $\cdot$ dm^{-3}) di-*t*-butyl-ketone. Prior to photolysis they were deoxygenated by purging with helium. The temperature range of the kinetic experiments was limited by the requirement of a fast decarbonylation (4) compared to termination (1, 2, 5-7) at the lower (−25 °C), bad signal/noise ratio (partly due to evolving CO gas) at the upper end (107 °C).

3.2. *Kinetic ESR. experiments.* The experimental arrangement and the general procedures have been published previously [13] [14] [23]. In this study a flat reaction quartz cell of 0.63 mm optical path length was used, which corresponded to a maximum light absorption of 60% in the whole $n\pi^*$ transition band. The solutions flowed continuously through the cell. The reaction volume of (93 ± 1) mm^3 and the flow rate of 5 mm$^3 \cdot$ s^{-1} lead to a dwell-time in the irradiation zone of $\Delta t = (18.5 \pm 0.5)$s. The sample temperature was measured by a thermocouple, which was protected by a glass capillary and located in the liquid about 2 cm above the irradiation zone. This distance was found to lead to an underestimate of the real sample temperature of *ca.* 3 K for usual light intensities [14] [23] and temperatures > 10 °C. To eliminate this source of error, the irradiation heat was reduced by insertion of a UV.-transparent glass (UG 11, *Schott & Gen.*) in the optical path, and by diminishing the sector slot. This reduced quantum flux was used whenever the signal to noise ratio allowed (typically for temperature < 30 °C, $\eta > 3$ mPa $\cdot$ s), otherwise the temperature reading [23] was augmented by 3 K. The inherent time constant of the ESR. spectrometer (*Varian* E-9) was measured and found to be determined by the phase sensitive detector of the 100 kHz amplifier, whose response behaviour may be characterized as follows: Decay and rise of a signal are identical and non-exponential. The halflife was approximately 105 µs, but there was no response within the first 15-20 µs. Only the tail had a roughly exponential shape (lifetime *ca.* 55 µs). The signal reached its final value after *ca.* 350 µs. This compares well with the factory-specified amplifier rise-time of 400 µs [26].

The time dependence of the *t*-butyl concentration R(t) was followed by monitoring the amplitude of the strongest transition of the ESR.-spectrum, that is the $K = 3/2$, $M = -1/2$ transition of the second-order pattern, and was recorded after averaging 4,000-20,000 on-off cycles, together with the base line of the spectrometer. *Figure 1* shows a typical experimental record of R(t) and of the baseline (R=O). R(t) was fitted by least squares to the theoretical rate law for the off-period,

$$R(t) = R(0) \cdot (1 + 2\,k_t\,R(0) \cdot t)^{-1} \tag{11}$$

where R(0) denotes the concentration at the end of the on-period. Since a steady state situation is reached by this time, R(0) may be determined from the steady state signal under continuous illumination. To avoid errors due to the inherent spectrometer time constant, incomplete decarbonylation at t=0, and sector error, the first part of the decay was discarded in the analysis (arrow). $2k_tR(0)$ was taken from the fitted curve. Usually the first 200 µs of the signal were not considered, but under extreme conditions, *i.e.* for low temp., high viscosities and low chopping frequencies, up to 2 ms were ignored. In all cases this corresponded to a small (< 15%) fraction of the observed decay time, and the superposition of the fitted and the experimental curve showed good agreement.

Absolute radical concentrations were determined as described elsewhere [14b] [27] [28]. Slight CIDEP-effects [29] in the spectrum of *t*-butyl were ignored. For alcoholic solvents and temperatures < 40 °C they are characterized by a decrease of absorption with increasing magnetic field and differ from those found in other media. The width and shape of the *t*-butyl transition was governed by experimental parameters (modulation amplitude 10^{-2} mT, microwave power 0.1 mW) and was found constant for all solvents and temp., with the exception of high-viscous ($\eta > 8$ mPa · s) alcoholic solvents, where temperature dependent line broadening in the second-order pattern was observed. For this case the signals were strongly overmodulated (modulation amplitude 0.25 mT), so that their lineshapes were also practically temperature independent. Thus, only signal amplitudes had to be calibrated. This procedure was considered to be more accurate than repeating the double integration of the signals at every temperature.

To exclude uncontrolled long-term effects, the rate constant for the termination of *t*-butyl in tetradecane was checked from time to time, and a value $2k_t = 3.3 \cdot 10^9$ dm^3 · mol^{-1} s^{-1} at an effective temperature of 25 °C was assumed as a relative standard value [23]. All rate constants given for other

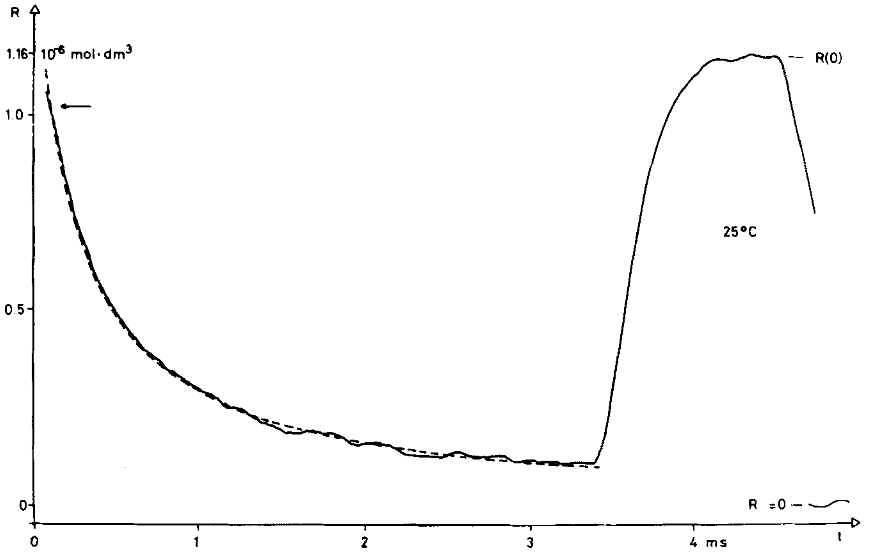


Fig. 1. *Time dependence of* t*-butyl concentration during intermittent photolysis of di-*t*-butylketone in hexadecane* (averaged from 15,000 scans). The line denoted R=0 at the lower right represents the spectrometer baseline

solvents are related to this value. Usually, the relative errors are *ca.* 10-25%, depending on the signal to noise ratio, but for highly activated viscosities this range may be exceeded, because of the error inherent to the temperature measurements (±2 K). The absolute error is estimated as ±50% and is mainly due to uncertainties in the determination of absolute radical concentrations.

3.3. *Steady state ESR. and product analysis.* In addition to the use of the kinetic ESR. method, rate constants in unbranched alkanes as solvents were also obtained from product yields and steady-state radical concentrations R(0). For complete decarbonylation (4) and negligible cage effects, the product yield is given by

$$\tfrac{1}{2}\,[\mathrm{R}(+\mathrm{H})+\mathrm{R}(-\mathrm{H})]+\mathrm{R}-\mathrm{R}=k_t\,\mathrm{R}(0)^2\cdot\Delta t \qquad (12)$$

where Δt denotes the dwell-time of the solution in the reaction cell. Since R(0) enters equations (11) and (12) differently, agreement of k_t values obtained by the two different techniques may be regarded as strong support for the accuracy of the procedures. For the determination of steady-state radical concentrations R(0) the same experimental arrangement as for kinetic ESR. was used. For the determination of product yields the irradiated solutions were collected, known amounts of benzene and isopentane were added to serve as internal references in the GLC. analysis. The gas chromatograph (*Carlo Erba* Fractovap 2101) was equipped with glass capillary columns (40 m Ucon LB 100 °C, 50 m OV-1, 250 °C). The detector sensitivity was calibrated for each solvent by comparing the signal-integrals of solutions containing known amounts of the expected products to those of the internal references. Relative integrals were evaluated electronically (*Infotronics*, Integrator CR-101) or by hand from the peak height and width. The chromatograms of the irradiated ketone solutions revealed the formation of isobutane, isobutene and hexamethylethane for all the solvents used (octane, decane, tetradecane) and for temperatures between 24 and 95 °C. Neither pivalaldehyde resulting from incomplete decarboxylation (4) or a cage reaction of the primary radical pair [3], nor products from an addition reaction to isobutene (10) were observed in significant concentrations, *i.e.* they amounted to less than 3% of the total product yield. This agrees with results of independent product studies for similar conditions [8] [19] [21] [22]. The absolute errors of the product yields is estimated to ±20%.

3.4. *Viscosity measurements.* Dynamic viscosities η in the range $0.2 < \eta < 50$ mPa · s were determined by *Ostwald* or *Ubbelohde* viscometry and by densitometry. Both densitometer and viscometers were thermostatted, the viscometers were calibrated over a large temperature range by at least three pure liquids of known viscosities [30] (*e.g.* unbranched alkanes, water, lower alcohols, phthalic esters or alkyl benzenes). Viscosities obtained by this technique are estimated to be accurate to ±5%. A thermostatted *Epprecht* viscometer (*Contraves* Rheomat 15, RM 15, rotating hollow or conically tipped cylinders) was used for measurements of viscosities in the range $10 < \eta < 100$ mPa · s. The dependence of shearing stress on the velocity gradient was studied by varying the speed of the rotating element, and was always found to be linear (*Newtonian* flow). At viscosities $\eta > 50$ mPa · s the alcoholic solvents used were supercooled liquids, and subjected to irreproducible, sudden crystallization. This did not affect the reproducibility of the results, but enforced repeated and relatively fast measurements. Since small temperature gradients (error < ±2K) within the liquid cannot be excluded, the error limits for $\eta > 50$ mPa · s may exceed ±5%.

4. Results. - The rate constants $2k_t$ for *t*-butyl termination (1) (2) determined by kinetic ESR. spectroscopy for twelve different solvents are given in *Tables 2* and *3* (3rd column), together with the temperatures of the measurements (2nd column). The listed values are averages over 1-10 independent runs. The rate constants clearly increase with increasing temperature for all solvents.

Figure 2 shows an *Arrhenius* plot of $2k_t$ for the solvents heptane, decane, dodecane and hexadecane. It is immediately evident that the rate constants increase not only with increasing temperature but also with decreasing solvent molecular weight. Further, within the indicated relative error (±15%), the data are well described by straight lines (correlation coefficients $r^2 > 0.98$). The data for octane and tetradecane are not displayed in *Figure 2* but fit smoothly into this picture. The

Table 2. *Termination rate constants of* t*-butyl radicals in non-alcoholic solvents*

Solvent	T[K]	$[10^9 \cdot dm^3 \cdot mol^{-1} \cdot s^{-1}]$			k_t^{exp}/k_t^{VAED}	k_t^{exp}/k_t^{SW}
		$2k_t^{exp}$	$2k_t^{VAED}$	$2k_t^{SW}$		
n-C_7H_{16}	294	7.9	8.8	8.4	0.89	0.95
	307	9.0	10.3	9.9	0.88	0.91
	325	11.8	12.4	12.3	0.96	0.96
	342	13.9	14.5	14.8	0.96	0.94
	349	15.5	15.4	15.7	1.01	0.99
	365	17.0	17.6	18.2	0.97	0.93
n-C_8H_{18}	297	6.8	7.7	7.4	0.88	0.92
	308	7.9	8.9	8.6	0.89	0.92
	325	8.8	10.9	10.7	0.81	0.83
	341	11.6	12.9	12.8	0.90	0.91
	345	11.4	13.4	13.2	0.85	0.87
	368	14.4	16.5	16.5	0.87	0.87
n-$C_{10}H_{22}$	295	5.6	5.2	5.1	0.94	1.11
	312	6.8	6.7	6.6	0.99	1.04
	328	8.7	8.3	8.1	1.04	1.07
	343	10.2	10.0	9.8	1.02	1.04
	354	11.8	11.3	11.1	1.04	1.06
n-$C_{12}H_{26}$	297	4.2	3.9	3.8	1.07	1.11
	308	4.6	4.7	4.6	1.02	1.0
	327	6.1	6.2	6.2	0.99	0.99
	346	7.4	7.9	8.1	0.94	0.92
	369	10.5	10.3	10.7	1.02	0.98
n-$C_{14}H_{30}$	297	3.4	3.1	2.6	1.11	1.33
	308	3.9	3.7	3.2	1.05	1.20
	326	5.5	4.9	4.6	1.11	1.20
	343	6.6	6.3	6.2	1.05	1.07
	369	9.8	8.7	9.2	1.12	1.06
n-$C_{16}H_{34}$	299	2.9	2.5	2.0	1.15	1.42
	305	3.2	2.8	2.3	1.13	1.37
	308	3.8	3.0	2.5	1.27	1.52
	311	3.4	3.2	2.7	1.08	1.27
	318	4.4	3.6	3.1	1.24	1.42
	323	4.6	3.7	3.4	1.19	1.34
	330	5.2	4.3	3.9	1.20	1.33
	343	6.3	5.3	5.0	1.20	1.26
	356	7.8	6.3	6.2	1.24	1.26
	366	9.1	7.2	7.2	1.27	1.26
CH_3CN	266	4.7	-	5.5	-	0.86
	280	5.4	-	6.5	-	0.84
	290	6.4	-	7.2	-	0.89
	293	6.7	-	7.4	-	0.90
	306	7.7	-	8.5	-	0.91
	320	8.8	-	9.6	-	0.91
	337	(11.4)	-	11.0	-	(1.04)
	349	(13.6)	-	12.0	-	(1.13)
Benzene	281	4.6	-	5.5	-	0.84
	293	5.8	-	6.2	-	0.94
	295	6.1	-	6.4	-	0.95
	302	6.6	-	6.8	-	0.97
	305	6.9	-	7.0	-	0.99
	314	7.3	-	7.6	-	0.96
	325	8.7	-	8.2	-	1.05

Table 2 continued

Solvent	T[K]	$[10^9 \cdot dm^3 \cdot mol^{-1} \cdot s^{-1}]$			k_t^{exp}/k_t^{VAED}	k_t^{exp}/k_t^{SW}
		$2k_t^{exp}$	$2k_t^{VAED}$	$2k_t^{SW}$		
	336	9.5	-	8.9	-	1.06
	345	11.0	-	9.5	-	1.16
	351	11.2	-	9.9	-	1.13
OMCTS	287	3.0	-	2.2	-	1.41
	293	3.3	-	2.5	-	1.32
	299	3.8	-	2.8	-	1.35
	315	4.9	-	3.8	-	1.28
	335	7.1	-	5.4	-	1.31
	338	7.6	-	5.7	-	1.34
	358	10.7	-	7.7	-	1.39
	376	14.2	-	9.9	-	1.43

termination constants in acetonitrile, benzene and OMCTS *(Table 2)* also reveal an increase of $2k_t$ with decreasing molecular weight for a given temperature, and give good straight lines ($r^2 > 0.99$) for each solvent in *Arrhenius* plots. However, for acetonitrile at temperatures $T > 325$ K significant deviations from linear *Arrhenius* behaviour are observed. For the alcoholic solvents 3 MP and *t*-ButOH/Pin, the departures from linearity are even more pronounced *(Figure 3)*. Small but significant deviations from second order kinetics in the time dependence of the *t*-butyl radical concentrations, and increased isobutane yields [8], lead us to believe that solvent reactions such as (8) cause the sudden increase of $2k_t$ in acetonitrile at elevated temperatures. However, the non-*Arrhenius* behaviour of $2k_t$ in alcoholic solvents is not due to such effects, and also holds for *t*-ButOH.

The yields of the products isobutane R(+H), isobutene R(−H) and hexamethylethane R-R are given in *Table 4* for the solvents octane, decane and tetradecane. Also listed are the stationary concentrations of *t*-butyl R(0) during the reaction, the ratio of disproportionation to combination P_d/P_c

$$P_d/P_c = \frac{1}{2}\frac{R(+H)+R(-H)}{R-R} \tag{13}$$

and the termination rate constants obtained from the product yields *via* (12). For comparison, we include termination rate constants obtained by kinetic ESR. *via* interpolation from the *Arrhenius* plots, and the ratios of the results of the two different methods.

As is evident from *Table 4*, the yields of isobutane and isobutene are very nearly equal. This confirms the complete decarbonylation of pivaloyl (4), and largely excludes side-reactions (8) (10). Further, the termination rate constants obtained from product yields agree with those measured by kinetic ESR. within the relative errors of product and radical concentration determinations. This indicates that the absolute errors of k_t are probably smaller than the ±50% estimated from the accuracy of the absolute radical concentrations. Finally, we note that the ratio of disproportionation to combination decreases with increasing temperature, as it is often found for alkyl radicals in liquids [1]. This agrees with

Table 3. *Termination rate constants of* t*-butyl radicals in alcoholic solvents*

Solvent	T[K]	$[10^9 \cdot dm^3 \cdot mol^{-1} \cdot s^{-1}]$			k_t^{exp}/k_t^{GM}	k_t^{exp}/k_t^{SW}
		$2k_t^{exp}$	$2k_t^{GM}$	$2k_t^{SW}$		
t-ButOH	287	1.73	2.24	0.59	0.77	2.9
	290	2.10	2.56	0.71	0.82	3.0
	294	2.38	2.97	0.86	0.80	2.8
	297	2.7	3.42	1.03	0.78	2.6
	299	3.1	3.65	1.11	0.85	2.8
	308	3.8	5.1	1.68	0.74	2.2
	310	4.6	5.4	1.83	0.84	2.5
	325	6.5	8.4	3.1	0.77	2.1
	339	8.9	11.8	4.5	0.75	2.0
	356	11.9	16.6	6.5	0.72	1.8
3 MP	248	0.31	0.32	0.033	0.96	9.3
	253	0.40	0.41	0.048	0.97	8.2
	263	0.66	0.75	0.11	0.89	5.6
	272	0.97	1.19	0.23	0.81	4.2
	282	1.35	1.9	0.46	0.71	3.0
	293	2.1	2.91	0.83	0.72	2.5
	295	2.4	3.14	0.93	0.77	2.6
	308	3.7	4.8	1.63	0.77	2.3
	323	6.7	7.2	2.74	0.94	2.5
	339	9.1	10.3	4.35	0.89	2.1
	356	13.2	14.3	6.44	0.93	2.1
	367	16.1	17.4	8.2	0.93	2.0
	380	18.5	21.1	10.3	0.88	1.8
t-ButOH/Pin 1:2	267	0.074	0.14	0.0043	0.53	17.2
	274	0.129	0.25	0.011	0.52	11.7
	281	0.21	0.4	0.023	0.52	9.1
	285	0.3	0.55	0.037	0.55	8.2
	294	0.57	0.92	0.082	0.62	6.9
	302	0.96	1.39	0.15	0.65	6.1
	310	1.23	2.0	0.25	0.62	4.9
	323	2.12	3.3	0.51	0.64	4.1
	327	2.17	3.8	0.62	0.57	3.5
	340	3.48	5.7	1.09	0.61	3.2
	345	4.1	6.5	1.32	0.63	3.1
	352	4.66	7.7	1.64	0.61	2.8
	357	5.3	8.8	2.0	0.60	2.7
	368	7.1	11.1	2.7	0.64	2.6
	378	9.2	13.8	3.6	0.67	2.6

independent observations for *t*-butyl in the same and other solvents [22] [25], and will be discussed in a subsequent paper [8].

Figure 4 and *5* are logarithmic *(Andrade)* plots of solution viscosities η *versus* reciprocal temperatures. Qualitative comparison of *Figure 4* and *5* with *Figure 2* and *3* reveals an inverse relationship between η and $2k_t$: η generally *decreases* with increasing temperature, and the plots for η and $2k_t$ have opposite curvatures for the alcoholic solutions. Further, for the unbranched alkanes, η *increases* with the molecular size. With the exception of hexadecane and tetradecane solutions at

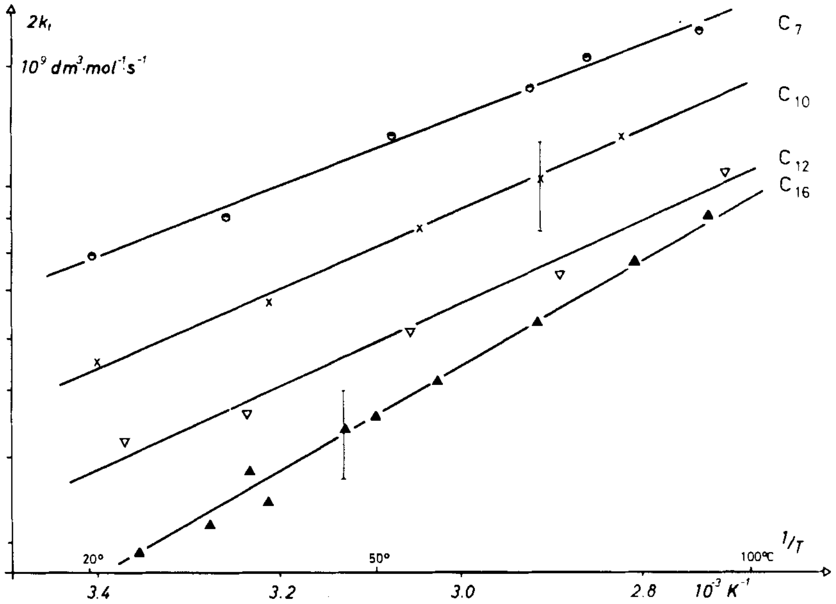


Fig. 2. *Termination rate constants of* t*-butyl in heptane, decane, dodecane and hexadecane solutions of di-*t*-butylketone*

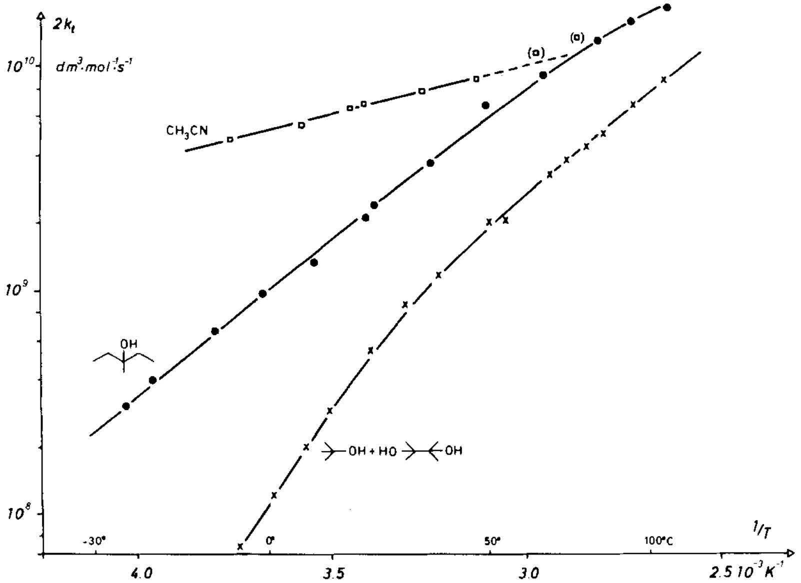


Fig. 3. *Termination rate constants of* t*-butyl in acetonitrile, 3-methyl-3-pentanol and* t*-butanol/pinacol solutions of di-*t*-butylketone*

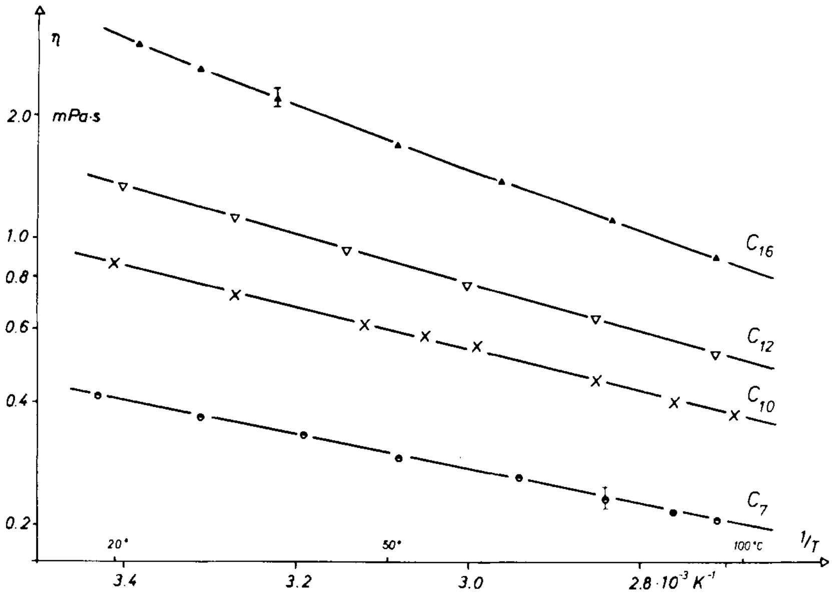


Fig. 4. *Dynamic viscosities of alkane solutions*

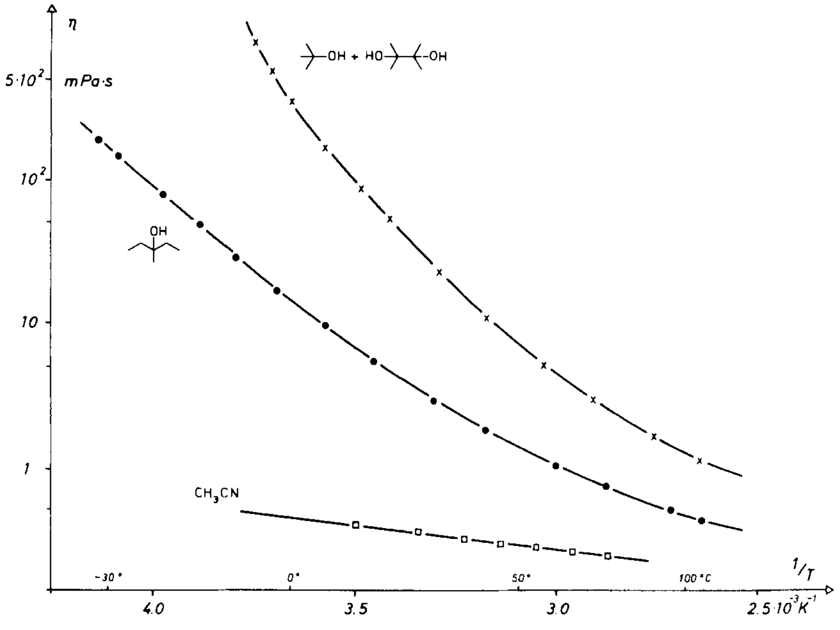


Fig. 5. *Dynamic viscosities of alcoholic and acetonitrile solutions*

temperature $<37\,°C$ and $<27\,°C$ respectively, the viscosities of all the non-alcoholic liquids are well described ($r^2 > 0.996$) by *Andrade's* law,

$$\ln \eta = \ln A_\eta + E_\eta/RT \tag{14a}$$

which is formally identical to the *Arrhenius* law

$$\ln 2k_t = \ln A_{kin} - E_{kin}/RT \tag{14b}$$

The occurence of slight deviations from the law (14a) for hexa- and tetradecane solutions near room temperature is also observed for η of the pure liquids [30], but within the absolute experimental error of ±5% and for temperatures $>25\,°C$ they may be neglected. For the alcoholic solutions, however, *(Fig. 5)* the *Andrade* law

Table 4. *Termination rate constants of* t-*butyl radicals from product analysis and steadystate ESR. in alkane solvents*

Solvent	T[K]	[10^{-2} mol · dm^{-3}]		[10^{-3} mol · dm^{-3}]	[10^{-7} mol · dm^{-3}]	P_d/P_c	[10^9 dm^3 · mol^{-1} · s^{-1}]		k_t/k_t^a
		R(+H)	R(−H)	R−R	R(0)		k_t	k_t^a	
n-C_8H_{18}	297	2.6	2.6	5.2	7.8	5.0	2.7	3.3	0.82
	326	2.5	2.4	5.8	6.5	4.1	3.8	4.7	0.81
	343	2.5	2.3	6.3	5.8	3.8	4.9	5.6	0.88
	367	2.3	2.0	6.1	4.6	3.6	7.2	7.0	1.03
n-$C_{10}H_{22}$	297	2.2	2.3	3.9	7.8	5.8	2.4	2.9	0.83
	325	2.3	2.2	4.5	6.9	5.0	3.0	4.2	0.71
	343	2.3	2.2	5.4	5.7	4.2	4.6	5.1	0.90
	367	2.2	2.0	5.4	4.8	3.8	6.2	6.6	0.94
n-$C_{14}H_{30}$	297	2.3	2.4	3.8	10.2	6.1	1.4	1.7	0.82
	326	2.4	2.4	4.7	8.0	5.1	2.4	2.7	0.89
	344	2.4	2.4	5.4	6.9	4.3	3.3	3.5	0.94
	368	2.3	2.2	5.5	5.8	4.0	4.5	4.7	0.96

[a]) Determined by kinetic ESR. and interpolation.

Table 5. *Values of the parameters* A_{kin}, E_{kin} *and* A_η, E_η *for non-alcoholic solvent*

Solvent	Termination rate constants, $2k_t$		Dynamic viscosities η		E_{kin}-E_η	$A_\eta \cdot A_{kin}$
	A_{kin}	E_{kin}	A_η	E_η		
	[10^{11}dm^3 · mol^{-1} · s^{-1}]	[kJ · mol^{-1}]	[10^{-2}mPa · s]	[kJ · mol^{-1}]	[kJ · mol^{-1}]	[10^9 mPa · dm^3 · mol^{-1}]
n-C_7H_{16}	4.9	10.10	1.51	8.04	2.1	7.4
n-C_8H_{18}	3.9	10.14	1.41	8.87	1.3	5.5
n-$C_{10}H_{22}$	5.0	11.17	1.62	9.71	1.5	8.1
n-$C_{12}H_{26}$	4.3	11.56	1.29	11.34	0.2	5.6
n-$C_{14}H_{30}$	8.2	13.67	0.81	13.56	0.1	6.6
n-$C_{16}H_{34}$	13.9	15.34	0.93[a])	14.0[a])	1.3	12.9
CH_3CN	2.0	8.33	2.42	6.61	1.7	4.8
Benzene	3.7	10.16	1.63	8.76	1.4	6.0
OMCTS	20.2	15.64	0.68	14.23	1.4	13.7

[a]) Strictly valid only for temperatures > 35 °C.

Table 6. *Values of the parameters* A_{kin}, E_{kin}, T_0 *and* A_η, E_η, T_0 *for alcoholic solvents*

Solvent	Termination rate constants 2 k_t				Dynamic viscosities η				E_{kin}-E_η	$A_\eta \cdot A_{kin}$
	A_{kin}	E_{kin}	T_0	r^2	A_η	E_η	T_0	r^2		
	$[10^{11} \cdot dm^3 \cdot mol^{-1} \cdot s^{-1}]$	$[kJ \cdot mol^{-1}]$	[K]		$[10^{-2} \cdot mPa \cdot s]$	$[kJ \cdot mol^{-1}]$	[K]		$[kJ \cdot mol^{-1}]$	$[10^9 \cdot mPa \cdot dm^3 \cdot mol^{-1}]$
t-ButOH	1.43	3.29	197	.996	1.21	5.10	191	.999	– 1.8	1.7
3 MP	2.08	3.62	198	.998a)	1.63	5.36	178	.999d)	– 1.7	3.4
	$1.18 \cdot 10^3$	26.5	-	.998b)	$3.04 \cdot 10^{-6}$	45.4	-	.998e)	– 18.9	$(3.6 \cdot 10^{-3})$
t-ButOH/	3.82	6.23	180	.999	0.95	7.43	189	.999	– 1.2	3.6
Pin 1:2	$3.52 \cdot 10^6$	49.5	-	.999c)	-	-	-	-	-	-

a) For $T > 293$ K; b) For $T < 340$ K; c) For $T \leq 295$ K; d) For $T \geq 270$ K; e) For $T < 270$ K.

is clearly inadequate. For such cases, it is often convenient to introduce solvent specific reduced temperatures $T-T_0$ [31] [32]:

$$ln\ \eta = ln\ A\eta + E_\eta/R(T-T_0) \tag{14c}$$

The *Arrhenius* law may be modified in analogous manner:

$$ln\ 2k_t = ln\ A_{kin} - E_{kin}/R(T-T_0) \tag{14d}$$

The parameters A_{kin}, E_{kin} and A_η, E_η listed in *Tables 5* and *6* were obtained from the experimental k_t *(Tables 2-4)* and η values by least square fits to eqs. (14a-d). For the non-alcoholic solvents *(Table 5)* $T_0 = 0$ K was assumed, and for the unbranched alkanes the rate constants from kinetic ESR. and product analysis were combined (relative weights 4:1). For the alcoholic solvents *(Table 6)*, T_0 was determined by optimizing the correlation coefficient in repeated linear regression calculations with varied values of T_0. For those alcohols (*e.g.* 3MP) where both the original (14a, b) and the modified (14c, d) laws gave adequate fits to the experimental data, parameters for both types of expressions are given in *Table 6*. Also listed are the correlation coefficients and, if necessary, the upper or lower temperatures for which the set of parameters is valid.

As apparent from column 6 of *Table 5*, the activation energies of the rate constants E_{kin} and of the bulk viscosities E_η are very nearly equal for non-alcoholic solvents. On the average, E_{kin} exceeds E_η by 1.2 ± 0.7 kJ · mol^{-1}. Further, the products $A_{kin} \cdot A_\eta$ depend only slightly on the solvents, considering the large possible systematic errors inherent in the frequency factor determinations. These findings indicate a correlation

$$2k_t \sim T^{1/2}/\eta \tag{15}$$

Solvent viscosity obviously governs the rates of *t*-butyl termination in non-alcoholic liquids. From the last columns of *Table 6* similar, but less pronounced trends for $E_{kin} - E_\eta$ and $A_{kin} \cdot A_\eta$ are noted for alcoholic solvents (only expressions with $T_0 = 0$ are considered).

5. Discussion. - 5.1. *Analysis for diffusion control.* An increase of the rate constant $2k_t$ with increasing solvent fluidity η^{-1} as observed here is customarily considered as strong indication for diffusion control of the reaction rate [2] [3] [9-15]. However, since a relation similar to (15) still holds for rate constants close to the diffusion controlled limit [3b] [33], the crucial question concerning the fraction ϕ of the total encounters that lead to reaction can only be answered after a more detailed analysis.

Since we may neglect short-time [34] or concentration [35] effects for our comparatively long radical lifetimes (*ca.* 0.5-5 ms) and low radical concentrations (10^{-6}-10^{-7} mol · dm^{-3}), we follow classical procedures [2] [3] [9] [11] [14] [18] [23] [36-42] and start from the *von Smoluchowski* equation in the form

$$k_t = \phi \cdot k_t^D = \phi \cdot 4 \cdot 10^{-3} \cdot \pi \cdot N \cdot D_{AXB} \cdot \rho \tag{16}$$

Here N denotes *Avogadro's* number, ρ the reaction distance, and D_{AXB} the sum of the diffusion coefficients of the two reactands A and X in the solvent B. A and X undergo reaction with the observed rate constant k_t at an encounter rate k_t^D. *Noyes* derived the theoretical expression [41] [42]

$$\phi = k_t/k_t^D = (1 + k_t^D/k_\infty)^{-1} \tag{17a}$$

where k_∞ represents the rate constant for an equilibrium molecular distribution which is not perturbed by reaction, *i.e.* the rate constant at infinitely fast translatory diffusion. However, *Logan* [33b] suggested that (17a) requires correction. Further, there is no unambiguous way to predict the hypothetical k_∞ for a given system. Therefore, we prefer a more empirical estimate of ϕ.

Generally, we expect ϕ to be determined by three contributions arising from steric ϕ_{st}, energetic ϕ_{en}, and spin statistical ϕ_{sp} effects

$$\phi = \phi_{st} \cdot \phi_{en} \cdot \phi_{sp} \tag{17b}$$

These three contributions may be estimated for *t*-butyl in the following way:

- ϕ_{st}: Although bulky substituents increase the radical lifetimes to persistency [4], small alkyl radicals terminate nearly equally fast in solution [42]. Together with the high absolute values of k_t, this indicates that steric effects are of minor importance for small alkyl radicals. Further, reorientational motions of the reacting species [8] [43-46] during the encounter in the solvent cage may compensate small steric shielding effects. This leads us to assume $\phi_{st} = 1$;
- ϕ_{en}: *Rehm & Weller* [47] found in fluorescence quenching experiments, that a diffusion controlled reaction occurred as soon as the free enthalpy of the reaction $\Delta\tilde{G}$ approached the limiting value $\Delta\tilde{G}_{lim} \lesssim -40$ kJ · mol^{-1}. For $-250 < \Delta\tilde{G} < -40$ kJ · mol^{-1}, the rate constants were independent of $\Delta\tilde{G}$, and for $\Delta\tilde{G} > -40$ kJ · mol^{-1} they dropped smoothly to lower values. It is instructive to apply these results to the termination reactions (1) (2), making use of the gas phase thermochemistry of *t*-butyl [48-50]. Taking a standard enthalpy of formation $\Delta H^0 = 37.2$ kJ · mol^{-1} and an entropy $S^0 = 302.2$ J · mol^{-1} · K^{-1} for *t*-butyl [47], and the corresponding data for the products [51a], we find $\Delta\tilde{G}^0(1) = -236$ kJ · mol^{-1}, for the recombination (1), and $\Delta\tilde{G}^0(2) = -221$ kJ · mol^{-1}, for the disproportionation (2). Obviously, both termination reactions are highly exergonic, and solvation effects are unlikely to alter the data significantly. Neglecting the possibility that the energetic limit for a diffusion controlled process $\Delta\tilde{G}_{lim}$ depends on the type of the reaction to some extent, we expect for *t*-butyl $\phi_{en} = 1$;
- ϕ_{sp}: As known from studies of cage effects [3] or electron transfer reactions [52] [53], the product formation from radical pairs is spin dependent. Usually $\phi_{sp} < 1$ [3] [14] [18] [36], since the three product triplet states are energetically inaccessible, and intersystem crossing of the radical pair to a singlet state [3b] during the encounter is improbable or unimportant for product yields [21]. Nevertheless, direct formation of triplet products is possible [53]. For our case, however, the disproportionation of *t*-butyl radicals to isobutene in its lowest triplet state (and isobutane) may be excluded: For this reaction a value of $\Delta\tilde{G}^0(2)^* \approx 130$ kJ · mol^{-1} is estimated using the singlet-triplet splitting of ethylene [54] and $\Delta\tilde{S} = 0$. Therefore, we assume in the following $\phi_{sp} = 1/4$, *i.e.* only encounters of radical pairs

with multiplicity $S=0$ (singlet) are allowed to react. With $\phi=\frac{1}{4}$ and for identical reactands (A = X), equation (16) becomes

$$2k_t^D=2\cdot 10^{-3}\cdot \pi \cdot N\cdot D_{AB}\cdot \rho \qquad (18)$$

If diffusion coefficients are not available, it is customary [2] [3] [9] [11] [37] [39] [40] to estimate them *via* the *Stokes-Einstein* equation in the form

$$D_{AB}=kT/6\pi r_A \eta \qquad (19)$$

and to identify the hydrodynamic radius r_A with half of the reaction distance. Combination of (18) and (19) leads to a simple relation between k_t^D and the solution viscosity

$$2k_t^D=\frac{R}{1500}\cdot T/\eta \qquad (20)$$

i.e. a relation similar to (15).

Figure 6 shows the experimental termination constants $2k_t$ of *t*-butyl radicals in unbranched alkane solvents plotted versus T/η (η calculated with the aid of (14a) and the parameters of *Table 5*). For comparison, results of *Hammond et al.* [18] for allyl and *E*-methallyl radicals in propene and *E*-2-butene solutions are included. Similarly, *Figure 7* depicts $2k_t$ for *t*-butyl in acetonitrile, benzene and alcoholic solvents as functions of T/η (η determined *via* eqs. (14a, c) and parameters given in *Tables 5* and *6*). The dotted lines in *Figure 6* and *7* represent the theoretically expected $2k_t^D$ according to eq. (20). The experimental rate constants are all clearly higher than those computed *via* (20). Furthermore, the linear dependence of $2k_t$ on T/η is not always obeyed: although this relation is well fulfilled for the non-associating liquids, *cf. Figure 6*, eq. (15), it is absent for the alcoholic solvents. Particularly noteworthy is the fact that the slopes of the straight lines found for $2k_t$ of *t*-butyl tend to increase with increasing molecular weight or size of the alkane solvent. A similar solvent size effect is observed in the series acetonitrile, benzene and OMCTS. This feature, and the nonlinear behaviour found for the alcoholic solvents, cannot be accounted for by simply changing constants in eqs. (18) or (19), *i.e.* by omitting the spin statistical correction ϕ_{sp} in (18), as discussed by some authors [2] [3] [37] [41b], or by replacing 6π in (19) by 4π to allow for the 'slip' rather than the 'stick' boundary condition in the hydrodynamic description of molecular diffusion coefficients [3] [14] [55] [56]. One might be tempted to postulate specific radical-solvent interactions influencing the reaction rates, as assumed by *Burkhart* [57] and *Hammond* [38] [18]. However, any complex formation of the radicals with the solvent would *increase* their hydrodynamic radii and consequently slow down their diffusional displacements (19). This would result in lower rate constants than calculated (20) for a free species. Just the opposite, namely higher rate constants are experimentally observed. Unreactive encounters caused by radical reorientations which are too slow [37] are also unable to explain the experimental results, since they again lead to values lower than the diffusion controlled limit. Although doubts have been expressed concerning the accuracy of the kinetic ESR. method [58], we do not believe that our experimental errors might have caused differences between theory and experiment by factors of 40 and more, as observed for the highly viscous alcohols. Such a discrepancy is far beyond the relative error, since for low viscous solvents theory and experiment

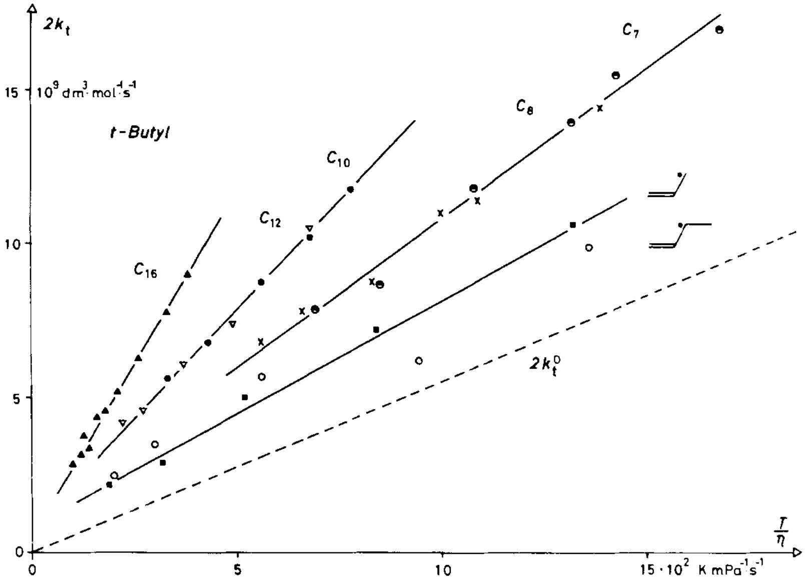


Fig. 6. *Comparison of the* von Smoluchowski-Stokes-Einstein *eq. (20)* (broken line) *with experimental rate constants of* t-*butyl in* n-$C_{16}H_{34}$ ▲, n-$C_{12}H_{26}$ ▽, n-$C_{10}H_{22}$ ●, n-C_8H_{18} ×, n-C_7H_{16} ◓, *and of allyl in propene* ■, *and* (E)-*methylallyl in* (E)-*2-butene* ○

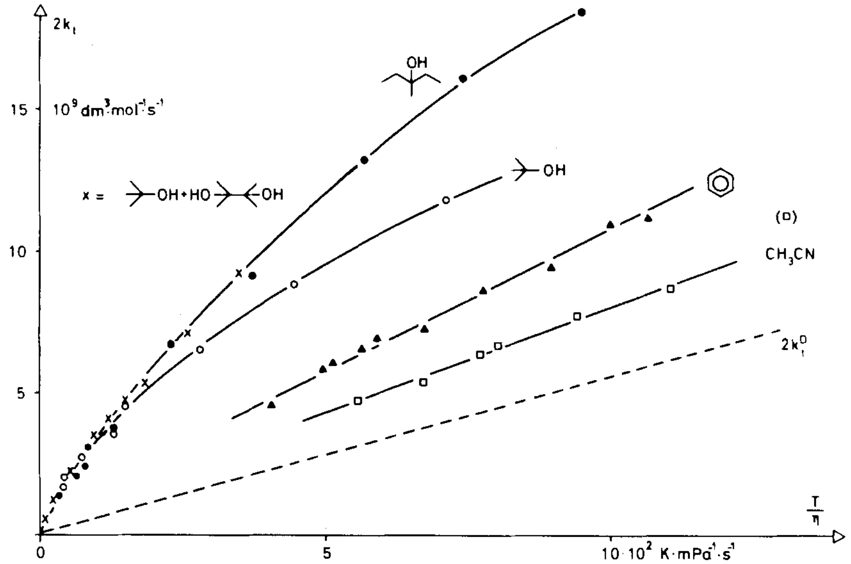


Fig. 7. *Comparison of the* von Smoluchowski-Stokes-Einstein *eq. (20)* (broken line) *with experimental rate constants of* t-*butyl in* t-*butylalcohol/pinacol, 3-methyl-3-pentanol,* t-*butylalcohol, benzene and acetonitrile*

agree within nearly a factor of two (*Fig. 6* and *7*). Further, the generally good agreement between the results of time resolved *(Table 2)* and steady state ESR. measurements combined with product yields *(Table 4)* points to an absolute precision of the rate constants which is better than ±50%. We rather believe that for small molecules the *Stokes-Einstein* equation (19) must be corrected in a solvent-specific way to give correct values. This view is supported by results of phosphorescence and fluorescence quenching studies [32] [34] [56] [59], and it is commonly accepted in the diffusion literature (for reviews see [60–66]).

Since no experimental diffusion data [30] [57] [60a] [62] [63] are available for *t*-butyl, we must use empirical recipes or semiempirical formulae to predict diffusion coefficients from solute and solvent properties [60] [61]. As it turns out, the predicted values depend strongly on the prescriptions used. Therefore, we adopt the following strategy to find out the most reliable procedure. Firstly, we choose a representative set of nine recommended [60] [61] or recent prescriptions [67–75] (chapter 5.2.). Subsequently, they are applied to estimate diffusion coefficients of isobutane or butane, which are taken as models for *t*-butyl (chapter 5.3). As far as possible, this is done for all solvents and two different temperatures (25 and 80 °C). Then, these diffusion coefficients are critically compared with each other (chapter 5.4). In particular, a set of relatively precise empirical values for the unbranched alkane solvents, and a discussion of basic features of some prescriptions allow us to sift the chaff from the wheat. Since for high solvent viscosities additional criteria are required, the best formulae are finally tested in a direct comparison with experimental diffusion coefficients of isobutene in dinonyl phthalate [76]. The constancy and value of the reaction diameter ρ of *t*-butyl is used as an additional, although indirect criterion for the precision of the diffusion coefficients (chapter 5.5).

The approximation of *t*-butyl by isobutane or butane is necessary, because the required macroscopic solute properties such as molar volume or heat of vaporization are unknown for the radical. In some cases, butane is favoured as model, since the regular behaviour of the unbranched alkanes allows rather precise determinations of its diffusion coefficient. Otherwise, isobutane is taken. The use of both isobutane or butane raises the question, to which extent diffusion coefficients depend on the mass and shape of the moving species.

The small mass difference caused by removing a hydrogen atom from the stable hydrocarbon to give a radical is equivalent to an isotope effect, and may be safely neglected [77]. We further neglect the (probably very small) volume difference between the radical and the diamagnetic molecules. The influence of the shape on diffusion [67] [78–80] seems more critical, but the situation is unclear. While *Hayduk et al.* [67] [78] find 'linear' molecules to diffuse faster than 'spherical', isochoric ones, liquid theory [79] and gas phase experiments [80] lead to opposite conclusions. Indications exist [67] [80], that especially for isobutane and butane the effect of branching is quite small. Further, as apparent from *Table 7*, unbranched alkanes tend to diffuse faster than their branched isomers under identical conditions. The differences are small, however, and we believe that the diffusion coefficients of isobutane and butane do not deviate from each other by more than ±20%.

Table 7. *Effects of branching on diffusion coefficients, D [10^{-5} cm^2 · s^{-1}], of alkanes in liquids at 25 °C*

Isomeric solutes	in CCl_4		in n-C_6H_{14}	
	D	ratio	D	ratio
Pentane	1.57[a])		4.59[b])	
		1.05		1.04
2-Methylbutane	1.49[b])		4.40[b])	
Hexane	1.50[a])		4.17[c])	
		1.20		1.15
2,2-Dimethylbutane	1.25[b])		3.63[b])	
Octane	1.26[a])		3.47[b])	
		1.12		1.03
Isooctane	1.13[b])		3.38[b])	

[a]) [81]; [b]) [82]; [c]) Average value from [67] [83], (4.13 and 4.21 resp.).

5.2. *Prescriptions for the prediction of mutual diffusion coefficients D_{AB} at low solute concentrations.* In the following we adopt the terminology proposed by *Albright & Mills* [84] for the terms mutual diffusion, intradiffusion, tracer diffusion and self-diffusion, and designate the different treatments by the initials of their authors.

5.2.1. *D_{AB} of unbranched alkanes in unbranched alkanes following* Hayduk & Ioakimidis (HI) [67]. Numerous measurements [31] [67] [68] [82] [83] lead to relatively accurate values of mutual diffusion coefficients. HI give a diffusivity-viscosity map designed for interpolation at 25 °C.

5.2.2. *D_{AB} of unbranched alkanes in unbranched alkanes following* Van Geet & Adamson (VA) [68]. *VA* develop an empirical nomograph for the prediction of self-diffusion coefficients as a function of temperature. At low solute concentrations mutual and tracer diffusion are equal and related to the self-diffusion coefficients D_{BB} of the solvent:

$$D_{AB} = (V_B/V_A) \cdot D_{BB} \tag{21a}$$

The ratio of the molar volumes of solute (V_A) and solvent (V_B) may be replaced by an empirical relation [68], yielding

$$D_{AB} = \frac{(n_B + T/150)}{(n_A + T/150)} \cdot D_{BB} \tag{21b}$$

where n_A and n_B are the number of carbon atoms in the solute and solvent molecular chains, respectively.

5.2.3. *D_{AB} in low viscous, non-associating solvents following* Spernol & Wirtz (SW) [69]. The often recommended [59] [66] [85] [86] expression corrects the *Stokes-Einstein* relation (19) to

$$D_{AB} \cdot \eta/T = k/6\pi r_A f \tag{22a}$$

by a microfriction factor f,

$$f = (0.16 + 0.4\, r_A/r_B)\,(0.9 + 0.4\, T_A^r - 0.25\, T_B^r) \tag{22b}$$

since (19) was derived for a macroscopic sphere diffusing in a continuum [87]. The dependence of f on the ratio of solute (r_A) and solvent (r_B) radii may be derived theoretically [88] [66], but (22b) was found empirically from experimental values of D_{AB} for non-associating, low viscous solute/solvent systems. The reduced temperatures

$$T_X^r = (T - T_X^f)\,(T_X^b - T_X^f)^{-1} \tag{22c}$$

are computed from the freezing T_X^f and boiling T_X^b points of solute or solvent (X = A or B), and serve as a rough measure for the interactive potentials between solute and solvent. The terms containing

T^r in (22b) may be understood as corrections for the 'stick' boundary condition used in the derivation of the *Stokes* law [55], which is inadequate for small, non associating solute molecules [89] [90].

The molecular radii are obtained from the molar volumes V_X:

$$r_X = (3\, V_X \chi / 4\pi N)^{1/3} \tag{22d}$$

where $\chi = 0.74$ is the space filling factor for close packed spheres.

5.2.4. *D_{AB} in low viscous, non-associating solvents following* Lusis & Ratcliff (LR) [70]. *LR* reason, that contrary to the hydrodynamic [87] and to the simple *Eyring* theory [91–93], the term $D_{AB} \cdot \eta/T$ depends on the molar volumes V_A and V_B:

$$D_{AB} \cdot \eta/T = 8.52 \cdot 10^{-10} \cdot V_A^{-1/3}\, [1.4 + (V_B/V_A)^{2/3}] \tag{23}$$

The right side of (23) was empirically determined by a fit to experimental D_{AB} values near room temperature. Eq. (23) is designed for cgs-units, the molar volumes are computed by the incremental method of *Le Bas* [71] [94].

5.2.5. *D_{AB} in low viscous solvents following* Wilke & Chang (WCh) [71]. The popular [60] [61] [70] [73–75] equation of *WCh* is also based on experimental diffusion data for low viscous systems:

$$D_{AB} \cdot \eta/T = 7.4 \cdot 10^{-10} \cdot V_A^{-0.6}\, (\kappa_B \cdot M_B)^{1/2} \tag{24}$$

Again, cgs-units and *Le Bas* molar volumes are required. M_B denotes the solvent molecular weight, and κ_B represents a solvent specific association parameter, which is 1.0 for non-associating solvents, 2.6 for water, 1.9 for methanol and 1.5 for ethanol. For alcohols, where κ_B is not reported,

$$\kappa_B = (\Delta H_B / \Delta H_{B\text{-}d})^{0.6} \tag{25}$$

[74]. In (25) ΔH_B denotes the enthalpy of vaporization of the alcohol and $\Delta H_{B\text{-}d}$ that of the alcohol's homolog, where a methyl group replaces the hydroxyl group, *e.g.* ethane is the homolog of methanol [95].

5.2.6. *D_{AB} in low viscous solvents following* Scheibel (Sch) [72]. The *Scheibel* equation is recommended by *Reid & Sherwood* [94]:

$$D_{AB} \cdot \eta/T = 8.2 \cdot 10^{-10} \cdot V_A^{-1/3}\, [1 + (3\, V_B/V_A)^{2/3}] \tag{26a}$$

Scheibel suggests that a change occurs in the diffusion mechanism when the molecular volume of the solute approaches that of the solvent, or becomes smaller. Except for methanol, water and benzene, he proposes

$$D_{AB} \cdot \eta/T = 17.5 \cdot 10^{-10} \cdot V_A^{-1/3} \tag{26b}$$

if $V_A < 2.5\, V_B$. For benzene the numerical constant in (26b) is $18.9 \cdot 10^{-10}$, and (26b) holds if $V_A < 2\, V_B$. Eqs. (26a, b) are valid for cgs-units and *Le Bas* molar volumes.

5.2.7. *D_{AB} in liquid/liquid systems following* Gainer & Metzner (GM) [73]. *GM* extend *Olanders* work [96], and develop expressions for the energy barriers which a diffusing molecule experiences. These are used for the prediction of D_{AB}, and are estimated from the density, viscosity and heat of vaporization of solute and solvent in their liquid state. The starting equation

$$D_{AB} \cdot \eta/T = k \cdot \xi_A^{-1} (N/V_B)^{1/3} \exp(E_{\eta B} - E_{DAB})/RT \tag{27}$$

results from an application of the *Eyring* theory [91] [92] to transport phenomena, where different activation energies $E_{\eta B}$ and E_{DAB} are assumed for the viscous and the diffusive flux. In the limiting case of self-diffusion, the exponential term is supposed to vanish ($E_{\eta B} = E_{DAB}$). Hence, the geometric parameter ξ_A may be evaluated from self-diffusion data, and usually [73] [93] a constant value $\xi_A \approx 6$ is found (see however [31] [64] [97]). $E_{\eta B}$ and E_{DAB} are estimated as follows: E_η is calculated from:

$$E_{\eta X} = RT \cdot ln(2.19 \cdot 10^{-5} \cdot \eta_X \cdot V_X^{2/3} \cdot M_X^{-1/2} \cdot T^{-3/2} \cdot \Delta U_X) \tag{28}$$

where ΔU_X represents the internal heat of vaporization (cgs-units). Both $E_{\eta B}$ and E_{DAB} shall arise from two distinct steps: firstly, a hole must form in the solvent lattice (E^h_{BB}), and subsequently a solvent (E^j_{BB}) or a solute (E^j_{AB}) molecule jumps into this hole:

$$E_{\eta B} = E^h_{BB} + E^j_{BB} \tag{29a}$$

$$E_{DAB} = E^h_{BB} + E^j_{AB} \tag{29b}$$

For pure liquids GM assume

$$E^j_{XX} = E^h_{XX} = \tfrac{1}{2} E_{\eta X} \tag{29c}$$

In a hydrogen bonding medium the jump energy E^j_{AB} may strongly depend on whether A itself is hydrogen bonding or not. For the former case, E^j_{AB} is split into two contributions, arising from purely dispersion forces $E^j_{AB\text{-}d}$, and purely hydrogen bonding forces $E^j_{AB\text{-}H}$:

$$E^j_{AB} = E^j_{AB\text{-}d} + E^j_{AB\text{-}H} \tag{29d}$$

The binary energies E_{AB} are approximated by [96]:

$$E_{AB} = (E_{AA} \cdot E_{BB})^{1/2} \tag{29e}$$

which yields for (29d)

$$E^j_{AB} = \tfrac{1}{2}\,(E_{\eta A\text{-}d} \cdot E_{\eta B\text{-}d})^{1/2} + \tfrac{1}{2}\,(E_{\eta A\text{-}H} \cdot E_{\eta B\text{-}H})^{1/2} \tag{30}$$

Further, the effects of the relative sizes of solute and solvent on transport are accounted for, and the final expression is

$$\begin{aligned} E_{\eta B} - E_{DAB} = \tfrac{1}{2} E_{\eta B} &- \frac{\xi_A}{\xi_B}\left[\frac{V_A^{1/3} \cdot V_B^{1/3}}{(V_A^{1/3}+V_B^{1/3})^2} \cdot E_{\eta A\text{-}H} \cdot E_{\eta B\text{-}H}\right]^{1/2} \\ &- \frac{\xi_A}{\xi_B}\left[\frac{2^{22}(V_A^{1/3} \cdot V_B^{1/3})^{12}}{(V_A^{1/3}+V_B^{1/3})^{24}} \cdot E_{\eta A\text{-}d} \cdot E_{\eta B\text{-}d}\right]^{1/2} \end{aligned} \tag{31}$$

The ratio of the total activation energy $E_{\eta X}$ for viscous flow (28) to $E_{\eta X\text{-}d}$, *i.e.* to the activation energy originating from dispersion forces only, is given by

$$E_{\eta X}/E_{\eta X\text{-}d} = \Delta H_X/\Delta H_{X\text{-}d} \tag{32}$$

where the vaporization enthalpies of the alcohol (ΔH_X) and its homolog ($\Delta H_{X\text{-}d}$) are as defined by *Bondi & Simkin* [95]. For non alcoholic liquids $E_{\eta X\text{-}H} = 0$ and $E_{\eta X\text{-}d} \equiv E_{\eta X}$.

5.2.8. D_{AB} *for gases in liquids following* Akgerman & Gainer (AG) [74]. *AG* delete the distinction between hydrogen bonding and dispersion forces and start from:

$$D_{AB} \cdot \eta/T = k\,\xi_A^{-1}(N/V_B)^{1/3}(M_B/M_A)^{1/2}\exp(E_{\eta B} - E_{DAB})/RT \tag{33}$$

The geometric parameter ξ_A is evaluated from the molar volumes

$$\xi_A = 6(V_A/V_B)^{1/6} \tag{34}$$

To calculate $E_{\eta B} - E_{DAB}$ they also start from (29a, b), but equate the jump energy of solvent molecules E^j_{BB} to the *full, experimental* activation energy of the solvent viscosity

$$E^j_{BB} = -\frac{R\,ln(\eta_2/\eta_1) + \tfrac{1}{2}R\,ln(T_1/T_2)}{T_1^{-1} - T_2^{-1}} \tag{35}$$

Further, they account for different probabilities of a solute and a solvent jump, and obtain:

$$E_{\eta \mathrm{B}} - E_{\mathrm{DAB}} = E^{\mathrm{j}}_{\mathrm{BB}} \left[1 - (E^{\mathrm{j}}_{\mathrm{AA}}/E^{\mathrm{j}}_{\mathrm{BB}})^{1/(\xi_{\mathrm{A}}+1)}\right] \tag{36}$$

The solute jump energy was found empirically from experimental diffusion data of various gases

$$E^{\mathrm{j}}_{\mathrm{AA}} = 24.59 \cdot \mathrm{M_A}^{-0.186} \tag{37}$$

with $E^{\mathrm{j}}_{\mathrm{AA}}$ in kJ · mol^{-1}.

5.2.9. D_{AB} *in liquid/liquid systems following* Akgerman (A) [75]. *Akgerman* uses the same set of equations as *AG*, but instead of (35) and (37):

$$E^{\mathrm{j}}_{\mathrm{XX}} = E_{\eta \mathrm{X}} - \frac{\mathrm{R}\, ln(\mathrm{T}/\mathrm{T_0})}{\mathrm{T_0}^{-1} - \mathrm{T}^{-1}} \tag{38}$$

$\mathrm{T_0}$ is taken to be 273 K, and $E_{\eta \mathrm{X}}$ is the *Andrade* activation energy for the viscosity of X. For $\mathrm{T} = \mathrm{T_0}$, the second term is replaced by $\mathrm{RT_0}$.

5.3. *Application of the predictive formulae.* - 5.3.1. *Assumptions:* The addition of 3 Vol % ketone to the solvent leads strictly speaking to a ternary diffusion system [98]. However, since the mole fraction of the ketone is small, it is expected to influence diffusion only little [60] [61] [99–101], except *via* changes in the bulk viscosity. Therefore, viscosities of the solutions were used.

Further, we approximated *t*-butyl by isobutane, or butane if necessary *(HI, VA)*. Properties *P* of the 1:2 molar mixture of *t*-ButOH/Pin were assumed to be given by

$$P = \tfrac{1}{3} P(t\text{-ButOH}) + \tfrac{2}{3} P(\text{Pin}) \tag{39}$$

if no experimental data were available.

5.3.2. *Viscosities.* Solution viscosities followed from (14a, c) and *Tables 5* and *6*. Since η of isobutane was not available, the solute viscosities required in the treatments of *A* and *GM* were graphically inter- or extrapolated from values given for isobutene [18].

5.3.3. *Molar volumes (Table 8).* Temperature dependent molar volumes as determined from experimental densities were used in the treatments of *SW* and *GM*, and in equation (21a) of *VA*. For isobutane, densities at saturation pressure were taken from [102], and were graphically extrapolated for T > 60 °C. In all other cases, the molar volumes were calculated from *Le Bas* increments [71] [94], which give V at the normal boiling point. As apparent from *Table 8*, experimental and calculated molar volumes agree well for those solvents and temperatures where a comparison is possible, *i.e.* for heptane at 100 °C, and acetonitrile, benzene and *t*-ButOH at 80 °C. The *Le Bas* molar volume of OMCTS was estimated.

5.3.4. *Caloric parameters (Table 9).* Vaporization enthalpies $\Delta H_{\mathrm{v}}(\mathrm{T})$ of isobutane were graphically inter- or extrapolated from data given in [102]. For the alcoholic solvents $\Delta H_{\mathrm{v}}(\mathrm{T})$ was computed [95], with a shielding effect of 5.86 kJ · mol^{-1} for each hydroxyl group. The vaporization/enthalpy of the homolog of the alcohol at its normal boiling point, $\Delta H_{\mathrm{v}}(\mathrm{T^b})$, was converted to the same reduced temperature $\mathrm{T_R}$ as the alcohol according to:

$$\Delta H_{\mathrm{v}}(\mathrm{T_R}) = \Delta H_{\mathrm{v}}(\mathrm{T^b}) \cdot (3 - 3\mathrm{T_R})\, 0.38 \tag{40a}$$

Table 8. *Molar volumes* V [$cm^3 \cdot mol^{-1}$] *from experimental densities and* Le Bas *increments for various liquids*

Liquid	V (experimental)a)				V *(Le Bas)*	Liquid	V (experimental)a)				V *(Le Bas)*
	25°	50°	80°	100 °C			0°	25°	50°	80 °C	
n-C_7H_{16}	147	151	157	161	163	CH_3CN	51	53	55	57	56
n-C_8H_{18}	161	166	172	176	185	Benzene	-	90	92	95	96
n-$C_{10}H_{22}$	195	200	206	210	229	OMCTS	-	314	323	335	~350
n-$C_{12}H_{26}$	229	233	240	245	274	*t*-ButOH	-	95	98	103	104
n-$C_{14}H_{30}$	260	266	274	280	318	3 MP	120	124	127	132	148
n-$C_{16}H_{34}$	294	300	309	314	363	*t*-ButOH/ Pin 1:2	110	114	117	120	109
						Isobutane	100b)	105b)	111b)	120b)	96

a) From solution densities; b) Pure liquid at saturation pressure.

Table 9. *Vaporization-enthalpies* ΔH_v [$kJ \cdot mol^{-1}$] *for various liquids at different temperatures*

Liquid	ΔH_v(T)	
	298 K	353 K
n-C_7H_{16}	36.6	32.8
n-C_8H_{18}	41.6	35.9
n-$C_{10}H_{22}$	51.5	48.3
n-$C_{12}H_{26}$	61.1	56.8
n-$C_{14}H_{30}$	71.1	68.0
n-$C_{16}H_{34}$	81.2	77.5
CH_3CN	34.6	32.8
Benzene	33.9	30.8
OMCTS	55.5	52.2

Liquid/ boiling point (T^b,[K])	ΔH_v(T), ΔH_v(T_R)a)		
	273 K	323 K	378 K
3 MP (394)	54.0	49.8	44.8
3,3-Dimethylpentane (359)	35.5a)	33.3a)	30.5a)
t-ButOH (356)	44.8	40.9	35.8
Neopentane (283)	26.3a)	24.3a)	21.6a)
Pinacol (448)	76.2	70.7	63.2
Hexamethylethane (379)	39.3a)	37.4a)	35.0a)
Isobutane (262)	20.6	17.2	13.2

a) At the same reduced temperature T_R as the alcoholic homolog.

Equation (40a) was combined with *Guldberg*'s rule for critical temperatures T_c in its simplest form [103]

$$T_R = T/T_c = 2T/3T^b \tag{40b}$$

For all non-alcoholic liquids, ΔH_v(T) at a given temperature was calculated *via* (40) from $\Delta H_v(T^b)$ as quoted in [51b]. If $\Delta H_v(T^b)$ was not available, it was determined using (40) and the difference of the standard enthalpies of formation in the gas and the liquid phase [51b]. Internal energies of vaporization ΔU_X(T) were estimated from

$$\Delta U_X(T) = \Delta H_v(T) - RT \tag{41}$$

5.3.5. *Further procedures.* In the diffusivity-viscosity map of *HI* a straight line was drawn for butane by interpolation between the lines for propane and pentane. Equations (21a,b) proposed by *VA* were both applied, but with different data sets: a) For (21a), self-diffusion coefficients D_{BB} of the unbranched alkane solvents were gathered from the measurements of *Ertl & Dullien (ED)* [31], or from rules given by these authors (octane). Further, experimental molar volumes of isobutane and of the alkane solutions were used: **This version is designated** *VAED*; b) In equation (21b), selfdiffusion coefficients from the nomograph of *VA* were inserted: **This version is designated** *VA*. In the treatment of GM $\xi_A = \xi_B = 6$ was assumed, and the activation energy $E_{\eta A}$ was determined from the viscosity of isobutene *via* (28). As a consequence of extrapolating the liquid state of isobutene over 90 degrees and more, $E_{\eta A}$ dropped rapidly to zero for temperatures >80 °C, and finally to negative values. This led to a discontinuity in the temperature dependence of the diffusion coefficients. Therefore, we fitted diffusion coefficients obtained for temperatures <80 °C to an equation analogous to (14d), and used this expression to calculate values for temperatures >80 °C. For the treatment of *AG* and *A*, the temperature dependent activation energies $E_{\eta B}$ of the alcohols were determined for intervals of 10 °C.

5.4. *Comparison of diffusion coefficients estimated for* t-*butyl.* Diffusion coefficients of *t*-butyl in various solvents are given in *Table 10* and *11* for 25 and 80 °C, respectively. As obvious from *Table 10*, the empirical models of *HI*, *VAED* and *VA* yield diffusion coefficients for the individual alkane solvents which are nearly equal at 25 °C. For 80 °C the treatments *VA* and *VAED* again yield very similar values *(Table 11)*. These findings, and the strong experimental foundation of the empirical treatments, indicate a reasonable absolute precision (*ca.* ±20%) for the diffusion parameters. Comparison of the values derived from the other, semiempirical models, reveals differences of up to 300%. Obviously, some of the treatments are of limited value. This view is reinforced if the data for the remaining solvents are considered: For acetonitrile, benzene and OMCTS, the estimated diffusion coefficients vary by somewhat more than a factor of 4, and for the alcoholic solvents we find absurd discrepancies. Some of these deviations can be understood from the basic structures of the predictive equations, or from the conditions for which the models were developed. In the following, we briefly discuss these aspects, in order to decide which models are particularly appropriate for the solvents acetonitrile, benzene, OMCTS and the alcohols. From the semiempirical formulae we note that the *Stokes-Einstein* relation (19) must be modified in two aspects, in order to predict correct molecular diffusion data: Firstly, the sizes (or molecular weights) of *both solute and solvent* molecules must be accounted for [68-75]. Secondly, the effects of different interactions between solute/solvent and solvent/solvent molecules should be incorporated [69] [71] [73-75], especially for systems where molecular associations play a role [60] [61] [76] [104-106]. The various treatments fulfill these requirements to different extents:

For non-associating liquids, *SW* explicitely correct the *Stokes-Einstein* equation according to the two principles. Numerical values for such corrections 1/f (full) are given as a function of solvent in *Table 12*. For the alkanes, where the trend of the molecular sizes is obvious, a truncated correction factor 1/f (trunc.) [32] [59] [60b] [66] [85] [86] is also listed. Here, the second parenthesis in (22b) is neglected, *i.e.* only the effects of the molecular sizes are accounted for. Clearly, this leads to considerably smaller corrections, especially for tetra- and hexadecane. For these solvents, 1/f (trunc.) yields D_{AB} values which are a factor of two lower than the empirical data from *HI*, *VAED* and *VA*. On the other hand, the diffusion coefficients calculated with the full correction compare favorably with these data, which we believe correct. Therefore, we conclude that even for non-hydrogen bonding

Table 10. *Estimated diffusion coefficients* D_{AB} [10^{-5} cm^{2}s^{-1}] *of* t-*butyl in liquids at 25 °C*

Solvent	Model[a])									
	HI	*VAED*	*VA*	*SW*	*LR*	*WCh*	*Sch*	*GM*	*AG*	*A*
n-C_7H_{16}	4.0	4.4	4.7	4.2	4.0	3.7	2.9	4.7	3.5	5.1
n-C_8H_{18}	3.5	3.7	3.9	3.5	3.2	3.0	2.2	4.0	2.9	4.5
n-$C_{10}H_{22}$	2.7	2.6	2.7	2.5	2.2	2.1	1.4	3.1	2.0	3.3
n-$C_{12}H_{26}$	2.0	1.9	1.9	1.8	1.5	1.5	1.12	2.6	1.56	2.8
n-$C_{14}H_{30}$	1.6	1.5	1.5	1.24	1.04	1.0	0.59	2.1	1.27	2.7
n-$C_{16}H_{34}$	1.35	1.17	1.13	0.93	0.76	0.76	0.41	1.8	0.96	2.1
CH_3CN	-	-	-	3.7	3.4	2.6	3.3	6.8	2.6	3.2
Benzene	-	-	-	3.1	2.4	2.3	2.2	3.9	2.1	2.5
OMCTS	-	-	-	1.3	1.05	1.23	0.57	1.8	0.96	2.4
t-ButOH	-	-	-	0.51	0.37	0.40	0.31	1.7	5.9	44
3 MP	-	-	-	0.51	0.43	0.48	0.33	1.65	3.6	21
t-ButOH/ Pin 1:2	-	-	-	0.055	0.040	0.053	0.033	0.54	5.4	96

[a]) *HI: Hayduk & Ioakimidis* [67]; *VAED: Van Geet & Adamson* [68] with data from *Ertl & Dullien* [31]; *VA: Van Geet & Adamson* [68]; *SW: Spernol & Wirtz* [69]; *LR: Lusis & Ratcliff* [70]; *WCh: Wilke & Chang* [71]; *Sch: Scheibel* [72]; *GM: Gainer & Metzner* [73]; *AG: Akgerman & Gainer* [74]; *A: Akgerman* [75].

Table 11. *Estimated diffusion coefficients* D_{AB} [10^{-5}cm^{2}s^{-1}] *of* t-*butyl in liquids at 80 °C*

Solvent	Model[a])								
	VAED	*VA*	*SW*	*LR*	*WCh*	*Sch*	*GM*	*AG*	*A*
n-C_7H_{16}	7.5	8.2	7.7	7.9	7.2	5.8	9.2	6.9	9.6
n-C_8H_{18}	6.8	7.2	6.9	6.7	6.2	4.7	8.2	6.0	8.7
n-$C_{10}H_{22}$	5.3	5.6	5.2	4.7	4.6	3.1	6.9	4.5	6.7
n-$C_{12}H_{26}$	4.1	4.4	4.2	3.7	3.6	2.2	6.0	3.7	6.2
n-$C_{14}H_{30}$	3.4	3.7	3.4	2.9	2.9	1.64	5.4	3.4	6.3
n-$C_{16}H_{34}$	2.9	3.0	2.8	2.3	2.3	1.22	4.8	2.7	5.3
CH_3CN	-	-	5.8	6.0	4.7	5.9	12.4	4.9	5.7
Benzene	-	-	4.8	4.9	4.6	4.5	8.0	4.4	5.3
OMCTS	-	-	3.4	3.0	3.6	1.7	4.5	2.9	4.0
t-ButOH	-	-	2.9	3.0	3.3	2.5	7.5	7.5	19
3 MP	-	-	2.9	2.8	3.1	2.1	6.4	6.7	17
t-ButOH/Pin 1:2	-	-	0.82	0.74	0.97	0.61	3.8	5.7	25

[a]) See footnote a of *Table 10.*

Table 12. *Microfriction corrections for the* Stokes-Einstein *equation following* Spernol & Wirtz

Solvent	1/f[a]) (full)	1/f (trunc.)	Solvent	1/f[a]) (full)
n-C_7H_{16}	2.3-2.2	1.9	CH_3CN	2.0-1.7
n-C_8H_{18}	2.6-2.5	2.0	Benzene	2.7-2.0
n-$C_{10}H_{22}$	3.0-2.9	2.1	OMCTS	3.8-3.4
n-$C_{12}H_{26}$	3.3	2.1	t-ButOH	3.0-2.0
n-$C_{14}H_{30}$	3.6	2.2	3 MP	2.8-2.3
n-$C_{16}H_{34}$	3.8-3.9	2.3	t-ButOH/Pin 1:2	2.8-2.2

[a]) Ranges given for the lowest - highest measured temperatures in *Tables 2* and *3.*

solvents, the different interactions between solute/solvent and solvent/solvent molecules are important.

LR only account for particle size effects.

Consequently, we expect their equation (23) to yield results similar to the truncated version of *SW*. Indeed, the D_{AB} values predicted *via* (23) for tetra- and hexadecane are too low in comparison with the empirical values. The *WCh* formula (24) also fails for tetra- and hexadecane in a nearly identical manner. (The association parameter κ is defined only for hydrogen bonding solvents. It is noteworthy that several modifications have been proposed for κ [74] [105-107], and its use for non-alcoholic solvents has been suggested [105] [106]).

The variant (26b) of the *Scheibel* relations applicable here neither allows for solvent size nor for molecular interactions. Replacing $V_A^{1/3}$ in (26b) by r_A following (22d) leads simply to a *Stokes-Einstein* relation where 6π is changed to 3.8π (3.5π for benzene), which is similar to the 'slip' boundary correction [3] [14] [55] [56]. This form of (26b) and the generally low D_{AB} values *(Sch, Tables 10, 11)* lead us to mistrust the *Scheibel* treatment.

The models of *GM, AG* and *A* differ from the other semiempirical treatments essentially by the exponential corrections which are thought to account for the different activation energies of viscosity and diffusion.

For the unbranched alkane solvents, acetonitrile, benzene and OMCTS, these corrections are relatively small, and depend markedly on the model *(Table 13)*. As a common feature, the corrections increase with increasing solvent size and increasing $E_{\eta B}$, and for the non-alcoholic solvents they vary only weakly with temperature, since the terms $E_{\eta B}$-E_{DAB} are nearly *(GM)* or entirely *(AG, A)* constant. For the alcohols, however, $E_{\eta B}$ depends strongly on the temperature (see *Fig. 5*). The changes in $E_{\eta B}$ enter directly into the equations of *AG* and *A* (35) (38), but are less important in the expression (28) used by *GM*. As a consequence, the exponential corrections of *A* and *AG* change dramatically with temperature *(Table 13)*. This in turn leads to physically absurd results: For *t*-ButOH/Pin the *AG* model predicts

Table 13. *Values of the exponential corrections* $\exp(E_{\eta B}\text{-}E_{DAB})/RT$ *in the models*a) *of* GM, AG *and* A

Solvent	Modela),b)		
	GM	*AG*	*A*
n-C_7H_{16}	1.6	0.88	1.3
n-C_8H_{18}	1.9	0.92	1.4
n-$C_{10}H_{22}$	2.6	0.96	1.6
n-$C_{12}H_{26}$	3.4	1.1	2.0
n-$C_{14}H_{30}$	4.4	1.28	2.7
n-$C_{16}H_{34}$	5.7	1.34	2.9
CH_3CN	1.5	0.78	0.95
Benzene	1.7	0.78	0.97
OMCTS	4.2	0.83	1.21

Solvent		Modela)		
		GM	*AG*	*A*
t-ButOH	25 °C	4.9	15.4	117
	80 °C	2.6	2.4	6.0
3MP	25 °C	5.1	8.1	46
	80 °C	3.2	2.4	6.0
t-ButOH/ Pin 1:2	25 °C	15.2	113	2000
	80 °C	5.9	6.5	28

a) See footnote a of *Table 10*; b) Values at 25 °C.

little change for 25 and 80 °C, and the *A* treatment actually yields *decreasing* values of D_{AB} with increasing temperature *(Tables 10* and *11)*. Since for *t*-ButOH/Pin and temperatures < 10 °C the *AG* model also predicts a negative activation energy for diffusion, we conclude that both models are inadequate for our purposes. Thus we discount the models of *Sch, AG* and *A*. The question remains, whether the model of *GM* or the treatments of *SW, LR* and *WCh* are more appropriate. Therefore, we test the equations of *SW* and *GM* with diffusion coefficients measured by *Houghton et al.* [76] for isobutene in dinonyl phthalate in a similar viscosity range ($9 < \eta < 700$ mPa · s) to that covered in this work. Ratios D^{exp}/D^{calc} of experimental to calculated diffusion coefficients for isobutene, as obtained with the equations of *SW* or *GM* and data quoted in [18] [76], are shown in *Figure 8* as a function of temperature. Obviously, both treatments fail to reproduce the experimental results accurately: The *GM* model yields diffusion coefficients which are to high by a nearly constant factor (2.5 – 3.3). On the other hand, the *SW* treatment underestimates the effective D_{AB} by factors of 4.4 to 15, and the differences increase with increasing bulk viscosity. The latter agrees with observations of *Dainton et al.* [32]. According to *Houghton et al.* [76], the *WCh* model breaks down even more distinctly (factors 11.5-44), and it is unlikely that the prescription of *LR* works any better.

We deduce from the above findings that for highly viscous solvents only the *GM* model yields tolerable results, whereas for low viscosities the treatments *SW, LR* and *WCh* are appropriate. Independent control of the arguments presented so far seems still desirable, however. Therefore, the following, final test is applied. We simply *assume ad hoc* that the termination of *t*-butyl is diffusion controlled, and calculate the reaction diameter ρ of *t*-butyl *via* the *von Smoluchowski*

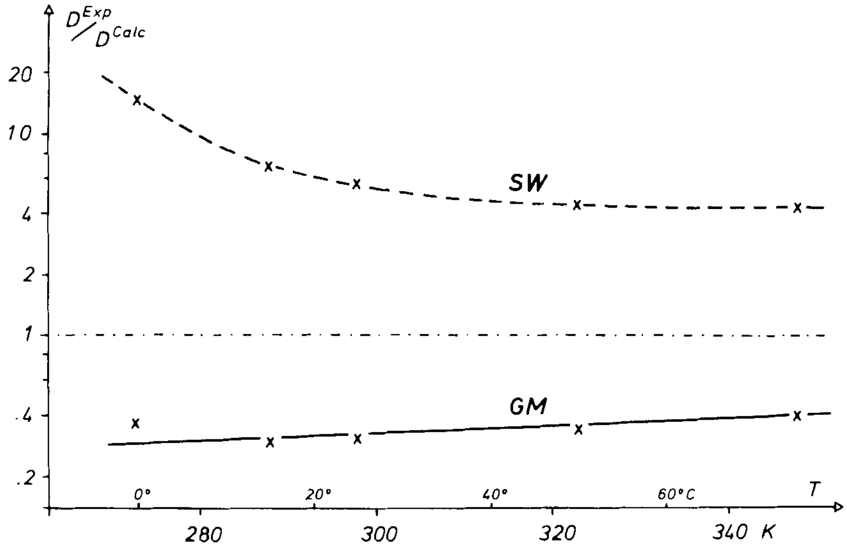


Fig. 8. *Ratios of experimental diffusion coefficients of isobutene in dinonyl phthalate to those calculated following* Spernol & Wirtz (SW) *and* Gainer & Metzner (GM)

equation (18) using interpolated experimental rate constants (eq. 14b,d and *Tables 5* and *6*), and the values of D_{AB} from *Tables 10* and *11*. Since ρ is an intrinsic property of the reactants, we expect it to be essentially solvent and temperature independent, if the termination is diffusion controlled. The expected constancy of ρ will thus provide a criterion for judging the quality of the diffusion coefficients.

5.5. *Reaction diameters of* t*-butyl*. Reaction diameters calculated as described above are listed in *Tables 14* and *15* for 25 and 80 °C, respectively. Obviously, ρ is strikingly independent of solvent and temperature, when it is computed with the empirical diffusion coefficients from *HI, VAED, VA*, and if the considerable relative errors for $2k_t$ and (possibly) D_{AB} are taken into account. These findings strongly support the concept of a diffusion controlled reaction. Further, the ρ values obtained with the diffusion coefficients from *SW, LR, WCh* and *Sch* reveal trends, which are easily rationalized with the limitations inherent in these treatments: For the low viscous solvents (heptane/dodecane, acetonitrile and benzene) ρ is generally constant within a factor of two and less, and the values are very similar to those found from the empirical diffusion coefficients. We ascribe this coincidence to the fact that these models are adjusted mainly for low viscous solvents. At higher medium viscosities, *i.e.* for tetra-, hexadecane and OMCTS, ρ seems significantly increased. Very probably this increase is an artifact arising from an underestimate of D_{AB}, and in accord with the structure of the equations, the *SW* treatment reveals the smallest, the *Sch* equation the largest scatter for ρ.

The enormous reaction distances derived for the alcoholic solvents are readily interpreted as a failure analogous to that observed for the *SW* treatment in *Figure 8*, *i.e.* the diffusion coefficients are far too small, and the errors increase with solvent viscosity (see *e.g.* *t*-ButOH/Pin at 25 and 80 °C). The analogy with *Figure 8* further extends to the ρ values obtained *via* the *GM* model: firstly, for a single solvent ρ is nearly temperature independent *(Tables 14* and *15)*. Secondly, ρ is always somewhat too low, if compared to the empirical treatments, *i.e.* the values of D_{AB} are too large. This trend seems nearly independent of the solvent. The extremely small ρ values obtained with the *AG* and *A* models for *t*-ButOH/Pin at 25 °C are clearly absurd, but it is remarkable that for 80 °C the *AG* treatment leads to a fairly constant reaction distance. This, and the fact that the *SW, LR, WCh, Sch, AG* and *A* models all yield a *smaller* scatter for ρ at 80 °C than at 25 °C (see the ranges in *Tables 14* and *15*), indicate once more, that these models give accurate diffusion coefficients only for low solvent viscosities. Clearly, the smaller scatter for ρ at 80 °C cannot be explained with errors in $2k_t$, since the latter *increase* with increasing temperature.

The absolute extent of diffusion control for the termination of *t*-butyl may be judged by comparing the values in *Tables 14* and *15* with theoretically calculated reaction distances. For this purpose, we adopt the experimentally verified [59] assumption, which is usually made in eq. (20) [2] [3] [23] [37] [38] [40], *i.e.* that the reaction diameter ρ may be identified with the hydrodynamic diameter $2r_A$ of the diffusing species.

The subject of hydrodynamic radii and their calculation has been discussed in some detail by *Edward* [86]. According to [86], hydrodynamic radii may be assumed to be temperature independent. The effective value of r_A may be estimated *via*

Table 14. *Reaction distances* ρ [10^{-8} cm] *of* t-*butyl in liquids at 25°C*

Solvent	Model[a])									
	HI	*VAED*	*VA*	*SW*	*LR*	*WCh*	*Sch*	*GM*	*AG*	*A*
n-C_7H_{16}	5.6	5.1	4.8	5.3	5.5	6.0	7.6	4.8	6.4	4.4
n-C_8H_{18}	5.0	4.7	4.5	4.9	5.4	5.8	7.7	4.3	6.0	3.9
n-$C_{10}H_{22}$	5.4	5.7	5.5	5.9	6.8	7.1	10.5	4.7	7.3	4.5
n-$C_{12}H_{26}$	5.4	5.8	5.7	6.0	7.2	7.3	9.7	4.2	6.9	3.8
n-$C_{14}H_{30}$	5.4	5.8	5.8	7.0	8.3	8.6	14.6	4.2	6.8	3.3
n-$C_{16}H_{34}$	5.8	6.7	7.0	8.5	10.4	10.4	19	4.5	8.2	3.8
CH_3CN	-	-	-	5.0	5.6	7.1	5.7	2.7	7.1	5.9
Benzene	-	-	-	5.3	6.8	7.2	7.4	4.2	7.9	6.4
OMCTS	-	-	-	7.6	9.3	7.9	17	5.4	10.2	4.1
t-ButOH	-	-	-	15	20	19	24	4.5	1.3	0.17
3MP	-	-	-	14	17	15	22	4.3	2.0	0.34
t-ButOH/ Pin 1:2	-	-	-	33	45	34	54	3.3	0.33	0.019
Range	5.0-5.8	4.7-6.7	4.5-7.0	4.9-33	5.4-45	5.8-34	5.7-54	2.7-5.4	.33-10.2	.019-6.4

[a]) See footnote *Table 10.*

Table 15. *Reaction distances* ρ [10^{-8} cm] *of* t-*butyl in liquids at 80°C*

Solvent	Model[a])								
	VAED	*VA*	*SW*	*LR*	*WCh*	*Sch*	*GM*	*AG*	*A*
n-C_7H_{16}	5.5	5.0	5.4	5.2	5.7	7.1	4.5	6.0	4.3
n-C_8H_{18}	4.8	4.6	4.8	4.9	5.3	7.0	4.0	5.4	3.8
n-$C_{10}H_{22}$	5.5	5.3	5.6	6.2	6.4	9.6	4.2	6.6	4.4
n-$C_{12}H_{26}$	5.5	5.1	5.4	6.1	6.2	10.2	3.7	6.0	3.6
n-$C_{14}H_{30}$	6.0	5.5	6.0	7.1	7.1	12.5	3.8	6.0	3.2
n-$C_{16}H_{34}$	6.9	6.6	7.0	8.8	8.7	16	4.2	7.3	3.8
CH_3CN	-	-	5.4	5.2	6.7	5.4	2.5	6.5	5.5
Benzene	-	-	6.5	6.3	6.6	6.8	3.8	7.0	5.8
OMCTS	-	-	7.7	8.6	7.3	16	5.8	9.0	6.6
t-ButOH	-	-	10.3	9.9	9.2	12	4.0	4.0	1.6
3 MP	-	-	11.4	11.9	10.9	16	5.2	4.9	1.9
t-ButOH/ Pin 1:2	-	-	16	18	13.6	22	3.5	2.3	0.54
Range	4.8-6.9	4.6-6.6	4.8-16	4.9-18	5.3-13.6	5.4-22	2.5-5.8	2.3-9.0	.54-6.6

[a]) See footnote *Table 10.*

van der Waals volume increments [86], yielding a good lower limit, or directly from molar volumes [59] [69], giving an upper limit. The real hydrodynamic volume is probably a sum of the molecule's *van der Waals* volume, and of the voids within the molecule which are inaccessible to the solvent. Since the *t*-butyl radical is too small to contain voids of size comparable to that of the solvent molecules, no solvent effects are expected from this side.

With the aid of the *van der Waals* volume increments [86] we obtain $\rho_{\mathrm{vdW}} = 5.3 \cdot 10^{-8}$ cm for *t*-butyl. Equation (22d) as applied by *SW* yields $\rho_{\mathrm{SW}} = 6.3 \cdot 10^{-8}$

cm, using the molar volume of isobutane (25 °C, *Table 8*). The method suggested by *Gorrell & Dubois* [59]

$$\rho_{GD} = 2\,r_X = (V_X/N)^{1/3} \tag{42}$$

leads to $\rho_{GD} = 5.4 \cdot 10^{-8}$ cm, using the prescribed *Le Bas* molar volume [71] [94]. From these three values we assume an average theoretical reaction distance for *t*-butyl,

$$\rho_{th} = 5.6 \cdot 10^{-8}\,\text{cm} \tag{43}$$

which we believe correct to within *ca.* ± 15%.

If we exclude the *Sch, AG* and *A* treatments, and discard the reaction distances obtained for the alcohols *via* the *SW, LR* and *WCh* models, the comparison of ρ_{th} with the experimental values *(Tables 14* and *15)* reveals a surprisingly good agreement: i) it is almost perfect, if only the empirical treatments are considered. They yield an average $\rho = (5.5 \pm 0.6) \cdot 10^{-8}$ cm; ii) it is good for the models of *SW, LR* and *WCh* for low viscous solvents, with *SW* giving the best results; iii) it is tolerable for the *GM* model and all solvents. Here, the average reaction distance $\rho = (4.2 \pm 0.8) \cdot 10^{-8}$ cm is smaller than ρ_{th}. It should be noted that for the unbranched alkane solvents the average deviation from ρ_{th} (factor 1.31) is very similar to that observed for the alcohols (factor 1.35).

The concept of an entirely diffusion controlled termination of *t*-butyl is further supported by the analogy of *Figure 8* and *9*: *Figure 9* shows ratios of experimental *(Table 3)* and calculated rate constant k_t^{exp}/k_t^{calc} for the alcoholic solvents as a function of temperature. The calculated rate constants were obtained *via* the *von Smoluchowski* equation (18), using ρ_{th} and diffusion coefficients computed following *SW* or *GM*. In the case of a diffusion controlled reaction, k_t^{exp}/k_t^{calc} becomes equivalent to D^{exp}/D^{calc}, since ρ_{th} and the experimental ρ (nearly) cancel out. Obviously, there is a striking analogy between *Figure 8* and *9*. However, clear solvent dependencies are apparent in the latter. Whilst the solvent specific behaviour of the ratios k_t^{exp}/k_t^{calc} obtained *via SW* is largely due to viscosity changes, unknown additional parameters seem to influence the differences in the ratios obtained *via GM*. These differences are comparatively small, however. Furthermore, they are nearly constant over the whole temperature range, and on the average they are similar to those found for the alkanes. We conclude, therefore, that they are largely due to uncertainties in the calculation of the diffusion coefficients, rather than to real deviations from a diffusion controlled reaction.

In *Figure 10* a representative choice of experimental rate constants for *t*-butyl is compared with calculated rate constants. (The full set of values of both k_t^{exp} and k_t^{calc} are given in *Tables 2* and *3*). The calculated rate constants were obtained with eq. (18) (43) and the best available diffusion coefficients: For the unbranched alkane solvents heptane to hexadecane (represented by the letters **A–F**, resp.) the model *VAED* of *Van Geet & Adamson* [68], combined with the data given by *Ertl & Dullien* [31] was used. The *Spernol & Wirtz* treatment [69] was applied for acetonitrile (**G**), benzene (**H**) and OMCTS (**J**). For lack of anything better, the equations of *Gainer & Metzner* [73] were used to compute the diffusion coefficients

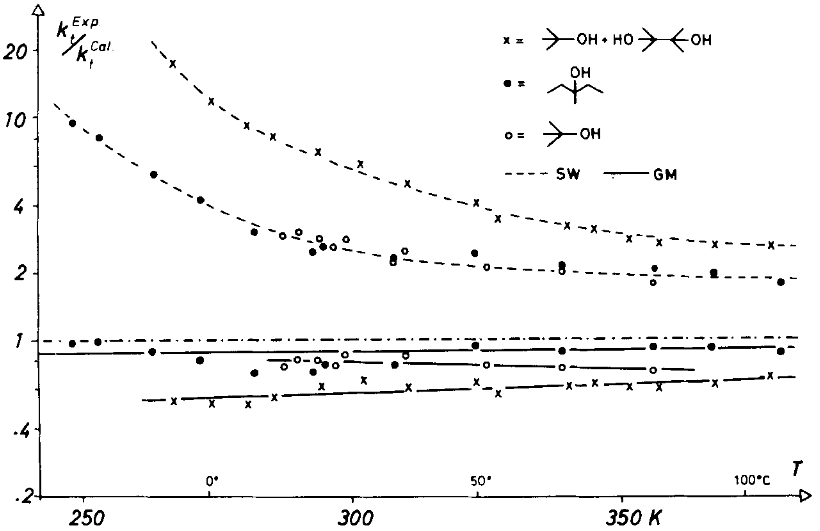


Fig. 9. *Ratios of experimental rate constants of* t*-butyl in alcoholic solvents to those calculated using* (18) (43) *and diffusion coefficients following* Spernol & Wirtz (SW) *and* Gainer & Metzner (GM)

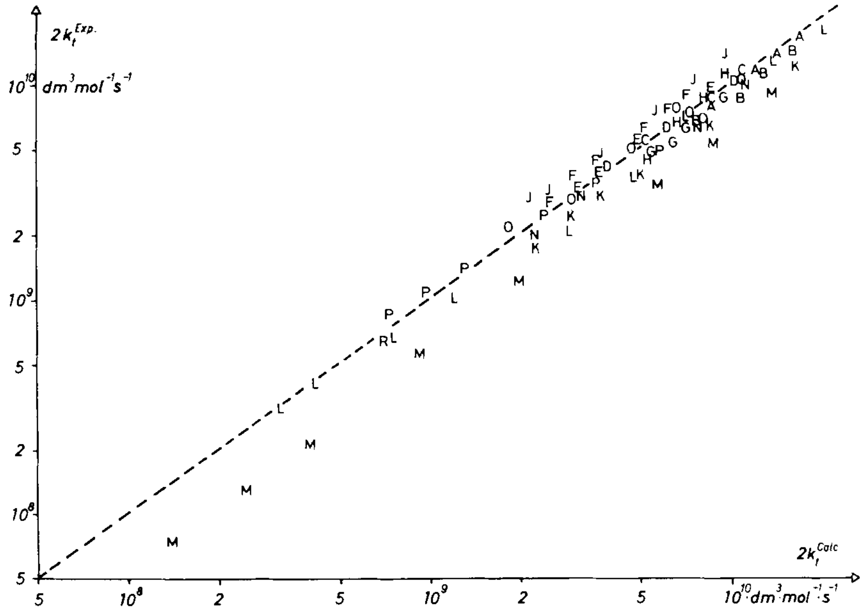


Fig. 10. *Experimental* vs. *calculated termination rate constants for:* t*-butyl in unbranched alkanes* (**A–F**), *acetonitrile* (**G**), *benzene* (**H**), *OMCTS* (**J**), *alcohols* (**K,L,M**); *allyl radicals in alkenes* (**N,O**); *methylol in methanol* (**P**), *and α-tetrahydrofuryl* (**R**) *in tetrahydrofuran* (for details see text)

in *t*-ButOH (**K**), 3 MP (**L**) and *t*-ButylOH/Pin (**M**). Further, we included rate constants of *Hammond et al.* [18], for allyl in propene (**N**) and (*E*)-methallyl in (*E*)-2-butene (**O**), and calculated the corresponding values *via* SW. The rate constants published by *Paul* [36] for methylol in methanol (**P**) and for α-tetrahydrofuryl in tetrahydrofuran (**R**) were compared to $2k_t^{calc}$ computed with experimental self-diffusion coefficients of the solvents [36] [85].

Obviously, the agreement between experimental and calculated rate constants is excellent, especially if we remember that $2k_t^{calc}$ is probably somewhat too large for *t*-butyl in the alcoholic solvents (**K**, **L** and **M**). Within the experimental and theoretical uncertainties, there are no indications of inefficient singlet radical-pair encounters, *i.e.* the radiation boundary condition in the *von Smoluchowski* equation is not required. The slight tendency to inefficient encounters (<20%) found previously [23] are probably an artifact due to the *SW* model used in the analysis, since this treatment tends to underestimate the diffusion coefficients at elevated viscosities. Further, it is probably not fully correct to cancel the hydrodynamic radius r_A defined by *SW* (22d) against the half reaction distance $\rho/2$, since the r_A of *SW* is slightly too large [86], especially at high temperatures. However, these effects change the calculated data given in [23] only little (< 15%), and do not affect the conclusions given there.

6. Conclusions. - The extensive comparison of experimental and calculated rate constants *(Figure 10* and *Tables 2* and *3)* leads us to believe that regardless of the chemical or physical property of the (inert) solvent, the self-termination reaction of *t*-butyl radicals is entirely diffusion controlled. This implies that for practically all conditions the rate constants may be predicted, provided the corresponding diffusion coefficients are available with sufficient accuracy. The following method for calculating rate constants seems correct: The *von Smoluchowski* equation (18) is used with a spin statistical factor $\phi_{sp} = \frac{1}{4}$, to account for the fact that only radical pairs in the electronic singlet state can undergo reaction.

The (isotropic) reaction diameter ρ of the radical is assumed to be solvent and temperature independent, in analogy to hydrodynamic radii. It is determined from molar (22d, 42) and molecular [86] volumes, and an average value from the different methods is taken.

For the diffusion coefficients specific radical solvent interactions are neglected (see however [57]), and the radical is approximated by its diamagnetic parent compound, which contains an additional hydrogen atom (or one less). The *Stokes-Einstein* equation (19) yields incorrect results, so diffusion coefficients must be calculated *via* empirical or semiempirical prescriptions (chapters 5.2.1.-5.2.9.). For non-associating, low viscous systems ($\eta \lesssim 3$ mPa · s) and for comparable sizes of solute and solvent, the *Spernol & Wirtz* treatment [69] seems to work best. Only special prescriptions like that of *Van Geet & Adamson* [68] for unbranched alkanes are slightly superior in the restricted range where they are valid. For the prediction of diffusion coefficients in highly viscous solvents ($\eta \gtrsim 10$ mPa · s), only the treatment of *Gainer & Metzner* [73] seems applicable, but with reservations: Whilst it predicts temperature dependencies almost perfectly, absolute deviations from the effective value may occur.

Recently, *Bennett & Summers* [108] found the termination constants of *t*-butyl in liquid isobutane and cyclopentane to be independent of the photolytic system for the radical generation. An analysis of the rate constants following [23] led them to conclude that the termination of *t*-butyl is completely diffusion controlled. This independent confirmation for *t*-butyl, and the fact that allyl type [18], methylol, tetrahydrofuryl [36] *(Fig. 10)* and benzyl radicals [109] show identical behaviour, strongly indicate that most sterically unhindered alkyl radicals terminate entirely diffusion controlled in the liquid phase. This means that the rate controlling step is diffusion into a cage, where - in contrast to the gas phase [48-50] - subsequent reorientational motions of the radicals [8] may overcome (small) sterical hindrance, and thus increase the reaction probability per encounter to unity. The experience obtained so far suggests that, at least for small alkyl radicals in low viscous solvents ($\eta \lesssim 3$ mPa · s), the proper inclusion of the spin statistical factor, and proper estimations of reaction diameter and diffusion coefficients allow prediction of termination rate constants with a comparable or even better accuracy than that inherent in many published experimental rate constants (see *e.g. Table 1*). However, extensive additional work is required to check these conclusions for other radical-solvent systems, especially for high viscosities and cases where molecular associations occur.

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REFERENCES

[1] *M.J. Gibian & R.C. Corley*, Chem. Rev. *73*, 441 (1973).
[2] *K.U. Ingold* in 'Free Radicals', ed. J.K. Kochi, Wiley, New York 1973, Vol. I, p. 37ff.
[3] a) *T. Koenig & H. Fischer*, ibid., Vol. I, p. 157ff.
b) *J.P. Lorand* in 'Progr. Inorg. Chem.', ed. J.O. Edwards & S.J. Lippard, Wiley, New York 1972, Vol. 17, pt. 2, p. 207ff.
[4] a) *D. Griller & K.U. Ingold*, Accounts chem. Res. *9*, 13 (1976).
b) *G.D. Mendenhall, D. Griller & K.U. Ingold*, Chemistry in Britain *10*, 248 (1974).
[5] a) *R.C. Sealy* in 'Electron Spin Resonance' (Specialist Periodical Reports), The Chem. Soc., London 1976, Vol. 3, p. 194ff.
b) *B.C. Gilbert & R.C. Sealy*, ibid., London 1974, Vol. 2, p. 188ff.
[6] *P. Neta*, Adv. phys. org. Chemistry *12*, 224 (1976).
[7] *A.T. Bullock*, Ann. Report, Progr. Chemistry *72B*, 88 (1975).
[8] *H. Schuh & H. Fischer*, Helv., to be published.
[9] *D.J. Carlsson & K.U. Ingold*, J. Amer. chem. Soc. *90*, 7047 (1968).
[10] *S.A. Weiner & G.S. Hammond*, ibid. *91*, 986 (1969).
[11] *G.B. Watts & K.U. Ingold*, ibid. *94*, 491 (1972).
[12] *G.B. Watts, D. Griller & K.U. Ingold*, ibid. *94*, 8784 (1972).
[13] *E.J. Hamilton, Jr. & H. Fischer*, J. phys. Chemistry *77*, 722 (1973).
[14] a) *H. Schuh, E.J. Hamilton, Jr., H. Paul & H. Fischer*, Helv. *57*, 2011 (1974).
b) *H. Schuh*, diploma thesis, University of Zürich 1974.
[15] *J.E. Bennett, J.A. Eyre, C.P. Rimmer & R. Summers*, Chem. Physics Letters *26*, 69 (1974).
[16] *H. Fischer* in 'Free Radicals', ed. J.K. Kochi, Wiley, New York 1973, Vol. II, p. 462ff.
[17] *E.J. Hamilton, Jr. & H. Fischer*, Helv. *56*, 795 (1973).
[18] *H.J. Hefter, C.S. Wu & G.S. Hammond*, J. Amer. chem. Soc. *95*, 851 (1973).
[19] *N.C. Yang, E.D. Feit, Man Him Hui, N.J. Turro & J.C. Dalton*, ibid. *92*, 6974 (1970).
[20] *H. Paul & H. Fischer*, Helv. *56*, 1575 (1973).
[21] *B. Blank, A. Henne & H. Fischer*, Helv. *57*, 920 (1974) and references cited therein.

[22] *P. Vesel,* diploma thesis, University of Zürich 1975.
[23] *H. Schuh & H. Fischer,* Int. J. chem. Kinetics *8,* 341 (1976).
[24] *M.J. Perkins & B.P. Roberts,* J. chem. Soc. Perkin II, *1974,* 297; *1975,* 77.
[25] *D. Griller & K. U. Ingold,* J. Amer. chem. Soc. *97,* 1813 (1975).
[26] *Varian, Analytical Instr. Division,* E-9 EPR System Manual, publication number 87-125-102, Palo Alto, California.
[27] *J.E. Wertz & J.R. Bolton,* 'Electron Spin Resonance', Mc Graw-Hill, New York 1972.
[28] *W. Schössler, D. Kirsch & G. Lassmann,* Z. Chem. *13,* 364 (1973).
[29] *P.W. Atkins, A.J. Dobbs & K.A. Mc Lauchlan,* J. chem. Soc. Faraday Transactions II, *71,* 1269 (1975).
[30] *Landolt-Börnstein,* ed. K. Schäfer, Vol. II, Part 5a (Transportphänomene), Springer-Verlag, Berlin 1969.
[31] *H. Ertl & F.A.L. Dullien,* Amer. Inst. chem. Eng. (AIChE) J. *19,* 1215 (1973).
[32] *F.S. Dainton, M.S. Henry, M.J. Pilling & P.C. Spencer,* J. chem. Soc. Faraday Trans. I, *1977,* 2433.
[33] a) *S.R. Logan,* J. chem. Soc. Faraday Trans. I, *1977,* 592.
b) *S.R. Logan,* Trans. Faraday Soc. *1967,* 1712.
[34] *T.L. Nemzek & W.R. Ware,* J. chem. Physics *62,* 477 (1975).
[35] *B.U. Felderhof & J.M. Deutch,* J. chem. Physics *64,* 4551 (1976).
[36] *H. Paul,* Chem. Physics *15,* 115 (1976).
[37] *P.B. Ayscough & R.C. Sealy,* J. chem. Soc. Perkin II *1973,* 543.
[38] *G.S. Hammond, E.J. Hamilton, jr., S.A. Weiner, H.J. Hefter & A. Gupta* in 'Proc. 23rd Int. Congr. Pure Appl. Chem.', Spec. Lect. Vol. IV, p. 257, 1971.
[39] *P.A. Carapelluci,* J. Amer. chem. Soc. *97,* 1278 (1975).
[40] *J. Hellebrand & P. Wünsche,* Z. Polymerforsch., Faserforsch. Textiltechnik *27,* 589 (1976).
[41] a) *R.M. Noyes* in 'Progress in Reaction Kinetics', ed. G. Porter, Pergamon Press, Oxford 1961, Vol. I, p. 129ff.
b) *R.M. Noyes,* J. Amer. Chem. Soc. *86,* 4529 (1964).
[42] *D. Griller & K. U. Ingold,* Int. J. chem. Kinetics *6,* 453 (1974).
[43] *K. Šolc & W.H. Stockmayer,* Int. J. chem. Kinetics *5,* 733 (1973).
[44] *E.L. Simmons,* Z. physik. Chem. N.F. *96,* 47 (1975).
[45] *J.M. Schurr & K.S. Schmitz,* J. phys. Chemistry *80,* 1934 (1976).
[46] a) *E.T. Denisov,* Bull. Acad. Sciences USSR, Div. Chem. Science *25,* 41 (1976) (Izv. Akad. Nauk SSSR, Ser. Chim. *1976,* 51).
b) *A.P. Griva, L.N. Denisova & E.T. Denisov,* Doklady phys. Chemistry *232,* 213 (1977) (Doklady Akad. Nauk SSSR *232,* 1343 (1977)).
[47] *D. Rehm & A. Weller,* Israel J. Chemistry *8,* 259 (1970).
[48] *K.Y. Choo, P.C. Beadle, L.W. Piszkiewicz & D.M. Golden,* Int. J. chem. Kinetics *8,* 45 (1976).
[49] *D.A. Parkes & C.P. Quinn,* J. chem. Soc. Faraday Trans. I *72,* 1952 (1976).
[50] *R.M. Marshall, H. Purnell & P.D. Storey,* ibid. *72,* 85 (1976).
[51] a) *F.D. Rossini, K.S. Pitzer, R.L. Arnett, R.M. Braun & G.C. Pimentel* in 'Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds', Carnegie Press, Pittsburgh 1953.
b) *Landolt-Börnstein,* eds. K. Schäfer & E. Lax, Vol. II, Part 4 (Kalorische Zustandsgrössen), Springer-Verlag, Berlin 1961.
[52] *H.J. Werner, Z. Schulten & K. Schulten,* J. chem. Physics *67,* 646 (1977).
[53] *H. Schomburg, H. Staerk & A. Weller,* Chem. Physics Letters *21,* 433 (1973).
[54] *S.L. Murov* 'Handbook of Photochemistry', M. Dekker, Inc., New York 1973.
[55] *H.J.V. Tyrell,* 'Diffusion and Heat Flow in Liquids', Butterworth, London 1961.
[56] *S. Bergström & B. Holmström,* Chemica Scripta *9,* 193 (1976).
[57] *R.D. Burkhart & R.J. Wong,* J. Amer. chem. Soc. *95,* 7203 (1973) and references cited therein.
[58] *D. Griller, B.P. Roberts, A.G. Davies & K.U. Ingold,* ibid. *96,* 554 (1974).
[59] *J.H. Gorrell & J.T. Dubois,* Trans. Faraday Soc. *63,* 347 (1967).
[60] a) *R.K. Ghai, H. Ertl & F.A.L. Dullien,* Amer. Inst. chem. Eng. (AIChE) J. *19,* 881 (1973) and the compilation of diffusion data cited therein.
b) *H. Ertl, R.K. Ghai & F.A.L. Dullien,* ibid. *20,* 1 (1974).
[61] *J. Simons & A.B. Ponter,* Canad. J. chem. Eng. *53,* 541 (1975).

[62] *P.A. Johnson & A.L. Babb,* Chem. Rev. *56,* 387 (1956).

[63] *D.M. Himmelblau,* Chem. Rev. *64,* 527 (1964).

[64] *H.G. Hertz,* Ber. Bunsen-Ges. phys. Chem. *75,* 183 (1971).

[65] *W. Hayduk & S.C. Cheng,* Chem. Eng. Sci. *26,* 635 (1971).

[66] *A.H. Alwattar, M.D. Lumb & J.B. Birks* in 'Organic Molecular Photophysics', ed. J.B. Birks, Wiley, London 1973, Vol. I, p. 403ff.

[67] *W. Hayduk & S. Ioakimidis,* J. chem. Eng. Data *21,* 255 (1976).

[68] *A.L. van Geet & A.W. Adamson,* Ind. Eng. Chemistry *57,* Nr. 7, 62 (1965).

[69] *A. Spernol & K. Wirtz,* Z. Naturforsch. *8a,* 522 (1953).

[70] *M.A. Lusis & G.A. Ratcliff,* Canad. J. chem. Eng. *46,* 385 (1968).

[71] *C.R. Wilke & P. Chang,* Amer. Inst. chem. Eng. (AIChE) J. *1,* 264 (1955).

[72] *E.G. Scheibel,* Ind. Eng. Chemistry *46,* 2007 (1954).

[73] *J.L. Gainer & A.B. Metzner,* Amer. Inst. chem. Eng. (AIChE) Intern. Chem. Eng. Symp. Series Nr. 6, p. 74 (1965).

[74] *A. Akgerman & J.L. Gainer,* Ind. Eng. Chemistry Fundam. *11,* 373 (1972); J. chem. Eng. Data *17,* 372 (1972).

[75] *A. Akgerman,* Ind. Eng. Chemistry Fundam. *15,* 78 (1976).

[76] *G. Houghton, A.S. Kesten, J.E. Funk & J. Coull,* J. phys. Chemistry *65,* 649 (1961).

[77] *R. Mills & K.R. Harris,* Chem. Soc. Rev. *5,* 215 (1976).

[78] *W. Hayduk & W.D. Buckley,* Chem. Eng. Sci. *27,* 1997 (1972).

[79] *F. Perrin,* J. Phys. Radium *7,* 1 (1936).

[80] *E. Grushka & P. Schnipelsky,* J. phys. Chemistry *80,* 1509 (1976).

[81] *R.K. Dewan & K.E. Vanholde,* J. chem. Physics *39,* 1820 (1963).

[82] *D.L. Bidlack, T.K. Kett, C.M. Kelley & D.K. Anderson,* J. chem. Eng. Data *14,* 342 (1969).

[83] *D.C. Douglass & D.W. Mc Call,* J. phys. Chemistry *62,* 1102 (1958).

[84] *J.G. Albright & R.J. Mills,* ibid. *69,* 3120 (1965).

[85] *H.S. Sandhu,* J. magn. Res. *17,* 34 (1975).

[86] *J.T. Edward,* J. chem. Educ. *47,* 261 (1970).

[87] *A. Einstein,* Z. Elektrochem. *14,* 235 (1908).

[88] *A. Gierer & K. Wirtz,* Z. Naturforsch. *8a,* 532 (1953).

[89] *C.-M. Hu & R. Zwanzig,* J. chem. Physics *60,* 4354 (1974).

[90] *D.R. Bauer, J.I. Braumann & R. Pecora,* J. Amer. chem. Soc. *96,* 6840 (1974).

[91] *S. Glasstone, K. Laidler & H. Eyring,* 'The Theory of Rate Processes', Mc Graw Hill, New York 1941.

[92] *F.H. Ree, T. Ree & H. Eyring,* Ind. Eng. Chemistry *50,* 1036 (1958).

[93] *J.C.M. Li & P.J. Chang,* J. chem. Physics *23,* 518 (1955).

[94] *R.C. Reid & T.K. Sherwood,* 'The Properties of Gases and Liquids', Mc Graw Hill, New York 1966.

[95] *A. Bondi & D.J. Simkin,* Amer. Inst. chem. Eng. (AIChE) J. *3,* 473 (1957).

[96] *D.R. Olander,* ibid. *9,* 207 (1963).

[97] *J. Lielmezs,* Z. physik. Chem. N.F. *91,* 288 (1974).

[98] *P.J. Dunlop, B.J. Steel & J.E. Lane* in 'Techniques of Chemistry', eds. A. Weissberger & B.W. Rossiter, Wiley, New York 1972, Vol. I, part 4, p. 205ff.

[99] *V. Sanchez & M. Clifton,* C.r. hebd. Séances Acad. Sci. Paris *282C,* 1093 (1976).

[100] *M. Harada, M. Tanigaki & W. Eguchi,* J. chem. Eng. Japan *9,* 85 (1976).

[101] a) *W. Reimschüssel & E. Hawlicka,* J. phys. Chemistry *78,* 2307 (1974).
b) *R. Haase, R. Kottmann & K.H. Dücker,* Z. Naturforsch. *30a,* 1084 (1975).

[102] 'Handbook of Chemistry & Physics', ed. R.C. Weast, 5th edition, CRC Press, Cleveland Ohio 1974.

[103] *R. Brdička,* «Grundlagen der phys. Chemie», VEB Deutscher Verlag Wissensch., Berlin 1971.

[104] a) *J.W. Moore & R.M. Wellek,* J. chem. Eng. Data, *19,* 136 (1974).
b) *R.D. Mitchell, J.W. Moore & R.M. Wellek,* ibid. *16,* 57 (1971).

[105] *C.J. King, L. Hsueh & K.-W. Mao,* ibid. *10,* 348 (1965).

[106] *R. Sitaraman, S.H. Ibrahim & N.R. Kuloor,* ibid. *8,* 198 (1963).

[107] *W. Hayduk & H. Laudie,* Amer. Inst. chem. Eng. (AIChE) J. *20,* 611 (1974).

[108] *J.E. Bennett & R. Summers,* J. chem. Soc. Perkin II *1977,* 1504.

[109] *M. Lehni, H. Schuh & H. Fischer,* to be published.