234. The Kinetics of the Bimolecular Self-Reaction of *t*-Butyl Radicals in Solution*)

II. Disproportionation/Combination Ratios[1])

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(19.VI.78)

Summary

Disproportionation/combination ratios P_d/P_c of self-reacting *t*-butyl radicals are determined as a function of solvent and temperature. The observed large solvent and temperature dependences are ascribed to anisotropic reorientational motions of the radicals during their encounter in the solvent cage. Results for other alkyl radicals are compatible with this concept.

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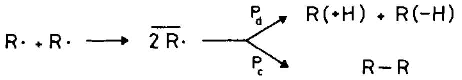
1. Introduction. - In a previous paper [1] we have shown that the self-termination rate constant k_t of *t*-butyl radicals R· in solution is governed by translational diffusion, *i.e.* every encounter of two radicals in the solvent cage [2] leads to reaction, provided the encounter pair $\overline{2R\cdot}$ is in an electronic singlet state. The products are either isobutane R(+H) and isobutene R(−H) from disproportionation (1), or 2,2,3,3-tetramethylbutane R—R from combination (2).

Scheme 1



(1)

(2)

In the present work, disproportionation/combination ratios P_d/P_c are determined by product analysis for various solvents and temperatures, and factors controlling the ratios [3] are discussed. The observed viscosity dependence of P_d/P_c is explained by a simple collision model which accounts for anisotropic reorientations of the radicals in the solvent cage. Literature values for P_d/P_c are given in *Table 1*. For the gas phase, $P_d/P_c \simeq 2.8$, independent of temperature within the considerable experimental scatter. Recent measurements in different laboratories [8] [9] point to a zero or small negative activation energy (-4 kJ · mol^{-1}) for the overall reaction rate constant k_t. Thus, the activation energies E_d and E_c for disproportionation and com-

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*) There was a misprint in the title of the 1st publication of this series. Please, correct the title of the 1st publication as given above. Red.

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

Table 1. *Disproportionation/combination ratios P_d/P_c for the self-reaction of* t*-butyl radicals*

Medium[a])		Temperature [K]	P_d/P_c	$(E_c - E_d)$[e]) [$kJ \cdot mol^{-1}$]	Ref.
Gas phase[b])		295-400	2.3	ca. 1	[4]
Gas phase		298	3.1	-	[5]
Gas phase		298	2.7	-	[6]
Gas phase		345	3.2	-	[7]
Gas phase		298	2.8	-	[8]
Gas phase		ca. 650	3.0	-	[9]
Benzene	(l)	293-333	4.5	0	[10]
Pentane	(l)	278	7.2	-	[11]
Benzene	(l)	298	4.8	-	[12]
TEP/DBPO[c])	(l)	253-353	7.5-3.0	6.3	[13]
TMS[d])	(l)	180-295	8.5-4.1	2.7	[14]
n-C_8H_{18}	(l)	297-367	5.0-3.6	4.3	[15]
n-$C_{10}H_{22}$	(l)	297-367	5.8-3.8	5.5	[15]
n-$C_{14}H_{30}$	(l)	297-368	6.1-4.0	5.5	[15]
Isobutene	(s)	90	500	-	[16]

[a]) (l) = Liquid, (s) = solid; [b]) Higher values were reported earlier, see notes in [3] [7] [11]; [c]) Triethyl phosphite/di-*t*-butylperoxide; [d]) Tetramethylsilane; [e]) Difference of 'activation energies' for combination E_c and disproportionation E_d.

bination of *t*-butyl radicals in the gas phase must be very small. In liquids, the ratios P_d/P_c are usually higher. Further, in most solvents, P_d/P_c clearly decreases with increasing temperature. This temperature dependence led *Griller & Ingold* [13] to conclude that in solution disproportionation and combination occur with different activation energies. Therefore, an *Arrhenius* plot of the termination rate constant k_t should be curved, and the *Arrhenius* parameters derived from it should have no exact significance [13]. However, since the rate controlling step in *Scheme 1* is formation of a radical pair $\overline{2R \cdot}$ *via* translational diffusion [1] [17], no information about the consecutive processes can be drawn from the values of k_t.

To explain the temperature and solvent dependence of P_d/P_c in liquids, we suggested earlier that viscosity may be a determining factor [15]. From a rough analysis of the data available at that time, a high-temperature/low-viscosity limit of $P_d/P_c = 3.0 \pm 0.5$ was suggested, which is similar to the gas phase value. The low-temperature/high-viscosity limit was estimated to be $P_d/P_c \sim 20 \pm 10$. This value is considerably lower than the ratio of 500 found in solid isobutene *(Table 1)*, indicating that the earlier analysis strongly underestimated medium effects at elevated viscosities. Nevertheless, the obvious large medium effects are in sharp contrast to the usual assumption that medium effects on P_d/P_c of alkyl radicals 'are quite small' [3].

2. Experimental Part. - *t*-Butyl radicals were generated *via* photolysis of solutions of di-*t*-butyl ketone (3 vol%). The solvents, sample preparation, most of the gas-chromatographic equipment and of the calibration procedure were the same as described earlier [1]. Signal-integrations were performed with a calculating integrator *Perkin-Elmer* M2. Prior to irradiation, three internal standards (pentane, hexane, heptane) were added to the solutions.

Deoxygenated solutions were driven in a continuous flow (0.5-5, typically 2 $mm^3 s^{-1}$) from a gas-tight syringe into a flat quartz irradiation cell (0.4 mm optical path length) *via* a thin Teflon hose. The cell had a mirror on its rear wall, and was surrounded by a closed *Dewar* vessel with quartz windows.

Table 2. *Product analysis of di-*t*-butyl ketone photolysis in various solvents*

Solvent	T[°C]	[10^{-3} mol · dm^{-3}]		[10^{-4} mol · dm^{-3}]			P_d/P_c[a])	*a*
		R(+H)	R(−H)	R−R	RCHO	TMP-1		
n-C_8H_{18}	25	3.7	3.6	6.85	0.2	-	5.4 (4.8)	1.03
	50	3.75	3.4	8.5	-	0.1	4.4 (4.2)	1.10
	87	3.65	3.2	8.8	-	0.2	4.1 (3.6)	1.13
n-$C_{10}H_{22}$	25	4.0	4.0	7.0	0.4	-	5.7 (5.8)	1.01
	50	3.3	3.2	7.2	-	-	4.6 (4.8)	1.03
	87	3.5	3.1	8.1	-	0.3	4.3 (3.9)	1.11
n-$C_{12}H_{26}$	25	3.85	3.95	6.5	0.6	-	5.9	0.99
	50	3.2	3.0	6.5	0.2	0.15	4.9	1.08
	69	3.15	2.75	6.7	0.1	0.2	4.7	1.13
	87	3.25	2.7	7.2	-	0.25	4.5	1.18
n-$C_{14}H_{30}$	25	4.05	4.0	6.35	0.9	-	6.4 (6.1)	1.04
	50	3.5	3.2	6.9	-	0.2	5.1 (5.1)	1.08
	87	3.7	3.0	7.7	-	0.4	4.7 (4.1)	1.20
n-$C_{16}H_{34}$	25	4.1	3.95	5.9	1.2	-	6.9	1.07
	50	4.1	3.9	7.6	0.7	0.2	5.4	1.06
	69	4.05	3.7	8.1	-	0.3	5.0	1.08
	87	4.25	3.7	8.45	-	0.4	5.0	1.13
OMCTS[b])	16.5	3.45	3.65	5.1	1.4	-	6.8	0.98
	69	3.5	3.35	7.85	-	0.2	4.4	1.03
	87	3.55	3.4	8.4	-	0.4	4.2	1.02
CH_3CN	−32	2.2	4.4	1.75	14.5	-	12.6	0.75
	−24	2.6	4.05	2.35	11.0	-	11.1	0.88
	− 5	3.65	4.6	3.95	5.0	-	9.2	0.89
	16.5	3.9	4.0	5.2	1.3	0.06	7.5	1.00
	46	3.9	3.7	5.85	0.3	0.1	6.7	1.06
	63	3.95	3.3	5.6	0.2	0.12	7.0	1.20
	69	3.8	2.9	5.0	-	0.12	7.6	1.30
t-ButOH/ Pin 1:2[c])	− 8.5	1.95	4.3	0.81	24	0.45	23.5	0.98
	− 6	3.6	7.8	1.6	40	0.8	22.0	0.91
	− 2	3.1	5.2	1.45	19	0.5	21.0	0.91
	3	4.15	5.7	2.15	12.5	0.5	19.1	0.91
	14	5.0	5.8	3.7	11.0	0.7	13.3	1.03
	25	10.0	10.1	9.7	13.5	1.7	10.1	1.10
	25	6.2	6.3	5.9	8.5	0.9	10.4	1.10
	49	10.6	9.6	12.7	5.2	1.0	8.3	1.14
	69	5.9	5.1	8.4	1.6	0.9	6.9	1.16
	86.5	2.6	2.3	4.7	0.7	0.4	5.5	1.13
	88.5	5.55	4.65	9.9	1.0	1.1	5.5	1.17
3-Methyl- 3-pentanol (3 MP)	−28.5	3.05	4.6	1.3	14	-	23.5	0.95
	−23.5	3.15	4.4	1.65	11.5	0.1	19.0	0.96
	−18	6.0	7.9	3.7	19	0.25	16.2	1.00
	−11	3.55	4.2	2.6	6.6	-	13.7	1.00
	8	3.6	4.0	3.65	3.7	-	9.9	0.99
	24.5	4.25	4.35	5.65	2.5	0.2	7.5	1.03
	46	4.40	4.30	7.15	1.3	0.25	6.1	1.04
	55	4.55	4.40	7.95	1.0	0.3	5.7	1.04
	70	4.25	4.0	7.85	0.7	0.3	5.4	1.07
	79	4.05	3.8	8.0	0.6	0.35	5.0	1.06
	83	3.85	3.5	7.7	0.5	0.35	5.0	1.09
	88	3.80	3.45	7.8	0.4	0.35	4.8	1.09
	98	3.75	3.35	7.8	0.3	0.45	4.7	1.10

[a]) Values in parentheses are interpolated from data given in [1].

[b]) Octamethylcyclotetrasiloxane.

[c]) *t*-ButOH/Pin 1:2, molar mixture 1:2 of *t*-butyl alcohol and pinacol.

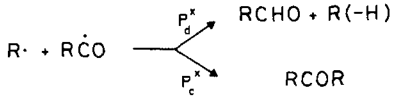
It was exposed to the filtered light ($265 < \lambda < 340$ nm, [1]) of a mercury high pressure lamp (*Philips* HPK 125 W). After passing through the cell the solutions were led through a capillary into a small septum sealed glass tube, outside the *Dewar* vessel. Solution samples were taken by a GLC. syringe through the septum. The collecting tube had a small lateral outlet extending into a long, thin hose, and was closed from the surrounding atmosphere by the out-flowing liquid. The *Dewar* vessel was thermostatted by passage of a temperature controlled ($-60 < T < 110°$) stream of nitrogen. Temperature was measured with the aid of a light-protected thermocouple fixed on the outside of the cell immediately above the irradiation zone. Small temperature gradients between the inside and the outside of the cell were determined in control measurements, and were corrected for. We estimate the temperatures given below to be accurate to ±2°.

Photolytic conversion of the ketone was less than 7%, typically 2.5%. The product ratios P_d/P_c were independent of the flow at rates > 1 mm^3 s^{-1}, and did not change with light intensity (when varied over a factor of 2). Since we were interested merely in relative product yields, no particular attention was paid to keep the conversion of the ketone equal in all runs, nor was a complete product balance [12] [14] attempted. Because of interference with the solvent, with the ketone, or small impurities, products containing more than eight carbon atoms were not determined. Product yields given below are averages from 3-10 independent runs. The error of the yields of the major products is estimated to be ±10%, and is mainly due to the limited reproducibility of the GLC.-injection process, and to uncertainties in the calibration. The yields of pivalaldehyde are less accurate (*ca.* ±20%), because the aldehyde was partially destroyed during analysis. The error of P_d/P_c is *ca.* ±15%, but may be larger in the alcoholic solvents at low temperatures, where the viscosity is strongly activated [1].

3. Results. - Product yields of the photolysis of di-*t*-butyl ketone RCOR in nine different solvents are given in *Table 2* for $-32 < T < 100°$. The primary steps of the reaction mechanism leading to *t*-butyl and pivaloyl $R\dot{C}O$ radicals are well known [1] [12] [14] [18] and not repeated here. As well as the products from the disproportionation (1) and combination (2) of *t*-butyl radicals, we found pivalaldehyde RCHO and small amounts (< 1 mol% of all products) of 2,4,4-trimethyl-1-pentene (TMP-1) and of 2,4,4-trimethylpentane (isooctane; not listed in *Table 2*). Pivalaldehyde results from the cross-reaction of *t*-butyl with pivaloyl *(Scheme 2)*. TMP-1 and isooctane are formed *via* addition (5a) of *t*-butyl to product isobutene (R(–H)), and by subsequent reactions (5b, 5c) of the resulting 2,4,4-trimethyl-2-pentyl radical ($R-\dot{R}(-H)$) with a second *t*-butyl radical [13] *(Scheme 2)*. 2,4,4-trimethyl-2-pentene (TMP-2) expected from disproportionation of *t*-butyl with $R-\dot{R}(-H)$ [16] was not observed (*i.e.:* (TMP-2) $< 0.2 \cdot$ (TMP-1)), nor was the combination product (*cf.* section 2). However, for statistical and steric reasons [3] [19], both products are anyway expected to be of minor importance.

As apparent from *Table 2*, the relative amounts of pivalaldehyde decrease markedly with increasing temperature. This trend is largely explainable in terms of the strongly activated rate of decarbonylation of $R\dot{C}O$ [18], which increasingly sup-

Scheme 2



(3)

(4)

$$R\cdot + R(-H) \rightarrow R-\dot{R}(-H) \qquad (5a)$$

$$R\cdot + R-\dot{R}(-H) \rightarrow R(-H) + \text{isooctane} \qquad (5b)$$

$$R\cdot + R-\dot{R}(-H) \rightarrow R(+H) + (\text{TMP-1}) \qquad (5c)$$

Table 3. *Solvent dependence of the pivalaldehyde formation*

Solvent	RCHO/R(+H)a) %	Solvent	RCHO/R(+H)a) %
n-C_8H_{18}	0.5	OMCTSb)	~ 3.5
n-$C_{10}H_{22}$	1.0	CH_3CN	~ 3
n-$C_{12}H_{26}$	1.6	3 MPb)	5.9
n-$C_{14}H_{30}$	2.2	t-ButOHb)/Pin 1:2	13.6
n-$C_{16}H_{34}$	2.9		

a) At or near 25°; b) For abbreviations see *Table 2.*

presses reaction (3) as the temperature is raised. Further, a pronounced solvent dependence of the yield of RCHO relative to isobutane R(+H) is observed *(Table 3)*. This strongly indicates that besides decarbonylation additional factors influence the formation of pivalaldehyde. At present we simply note that the ratios RCHO/R(+H) show a clear tendency to increase with microscopic solvent viscosity [1]. We will come back to this point later.

The consistency of the product concentrations given in *Table 2* may be checked [13], since according to reactions (1-5) the relation (6) holds.

$$a=\frac{\mathrm{R(+H)-(TMP\text{-}1)}}{\mathrm{R(-H)-RCHO+(TMP\text{-}1)}}=1 \tag{6}$$

As evident from the last column of *Table 2,* this relation holds in most cases within experimental error (*ca.* 15-20%). The slight increase of a with temperature

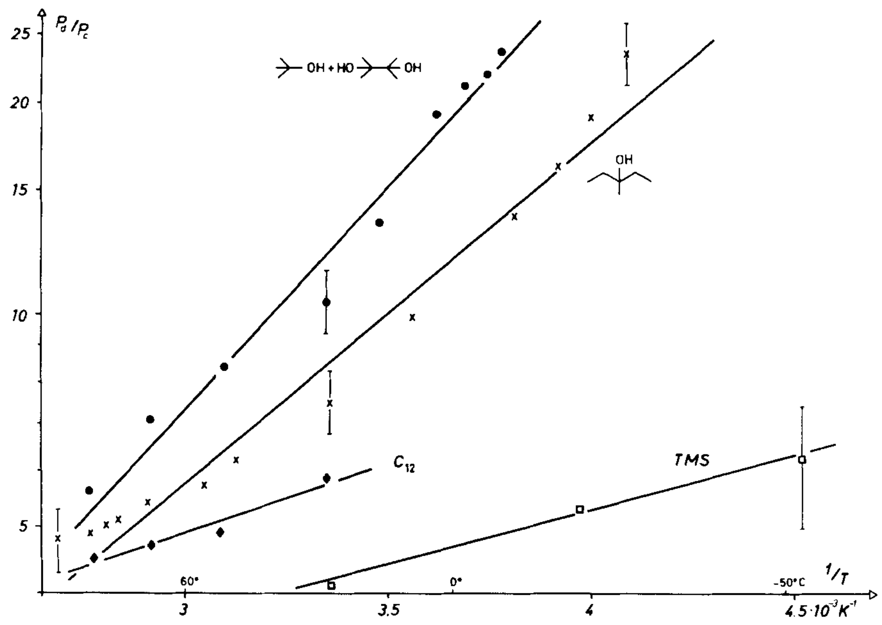


Fig. 1. *Disproportionation/combination ratios P_d/P_c of* t-*butyl in* t-*butyl alcohol/pinacol, 3-methyl-3-pentanol, dodecane, and in tetramethylsilane*

cannot be explained, except that values of $a < 1$ at, and below 0° are probably due to an underestimate of RCHO. For acetonitrile the deviations from unity are significant, however. We presume that solvent reactions occur. In particular, hydrogen abstraction by *t*-butyl at elevated temperatures would explain the abnormally high yields of isobutane, and also the previously observed deviations of the termination of *t*-butyl from second order kinetics [1].

The disproportionation/combination ratios P_d/P_c of *t*-butyl also given in *Table 2* are calculated according to (7a):

$$P_d/P_c = [R(+H) - (TMP\text{-}1)]/R-R \tag{7a}$$

$$P_d/P_c = [R(+H) + R(-H) - RCHO]/2R-R \tag{7b}$$

In earlier work [1] we used (7b) for conditions where RCHO could be neglected. The data for P_d/P_c obtained previously were fitted to *Arrhenius* expressions, and values interpolated there from are given in parentheses in *Table 2*. They agree with the new data within experimental error. These findings, and the considerable differences in ketone conversion (*ca.* factor 6), and in radical concentrations (*ca.* factor 4) the two sets of runs support the principal accuracy of the experimental method.

As apparent from *Table 2*, P_d/P_c decreases with increasing temperature in all solvents. Further, for a given temperature disproportionation increases with chain length in the n-alkane series. This solvent specific behaviour of the product ratios is even more pronounced in *Figure 1*, where *Arrhenius* plots are given for P_d/P_c in alcoholic solvents, dodecane *(Table 2)*, and in tetramethylsilane (TMS) [14]. Clearly, forced fits of the data to the *Arrhenius* law lead to solvent dependent slopes.

The differences in the 'activation energies' $E_c - E_d$ vary between 2.7 (TMS) and 12 $kJ \cdot mol^{-1}$ (*t*-ButOH/Pin)[2]. The latter value is considerably larger than any possible activation energy E_t of the overall termination reaction in the gas phase [8], and is larger than E_t in many solvents [1] [17] [18].

4. Discussion. - 4.1. *Previous concepts for the interpretation of P_d/P_c ratios.*

For a survey of the different concepts suggested for the interpretation of disproportionation/combination ratios of alkyl radicals, the reader is referred to the review of *Gibian & Corley* [3]. Several of these concepts may be ruled out as explanations for our findings:

The marked temperature dependence of P_d/P_c of *t*-butyl in the liquid phase, and the strong medium effects (*Tables 1, 2* and *Fig. 1*) largely exclude a correlation of P_d/P_c with the entropy difference between disproportionation and combination products [2a] [3] [6] [20]. Solvation effects [3] [11] [21] are not in accord with the increase of P_d/P_c with the chain length of the *n*-alkane solvents. Moreover, no indications exist for specific solvation effects influencing the radical mobility [1]. Further, since the termination reaction of *t*-butyl radicals is not activated in a classical sense (*cf.* section 2), it is improbable that changes in steric strain [19] govern the values of P_d/P_c observed here. On the other hand, a limited correlation between pressure and P_d/P_c [22] [23] cannot be excluded. Indeed, the trend of the internal pressure p_i [23-28] in *n*-alkane solvents is similar to that of P_d/P_c, *i.e.* p_i increases with the

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[2] *t*-ButOH/Pin = *t*-Butyl alcohol/Pinacol.

solvent chain length [28], and decreases slightly with increasing temperature [25]. For the alcoholic solvents it is difficult to obtain reliable estimates of p_i as a function of temperature and solvent, since experimental data are fragmentary [26-28] and calculation of p_i from vaporization energies is difficult [24-28]. However, a clear discontinuity in a possible relation between P_d/P_c and p_i occurs at the gas liquid change of phase: Here p_i changes by a factor of *ca.* 10^3, whilst P_d/P_c changes by a factor of two or less, as apparent from the values for elevated temperatures in *Tables 1* and *2* (except CH_3CN). This is in marked contrast to the more than fivefold change of P_d/P_c in liquids *(Table 2)* for a similar change in p_i [27] [28].

As mentioned above, we rather believe that the viscosity of the medium influences P_d/P_c [15]. In fact, the viscosities and activation energies E_η increase in the order TMS < dodecane < 3 MP < *t*-ButOH/Pin [1] [14], and qualitatively the same behaviour is observed for P_d/P_c *(Fig. 1)*. All other solvents fit into this picture (except CH_3CN). In the following we propose a simple collision model which ascribes this viscosity dependence of P_d/P_c to the anisotropy of the reorientational motions of the radicals during their encounter prior to reaction in the solvent cage. The reorientations enable transitions between unreactive configurations and those thought to be favourable for disproportionation and for combination. Because of the anisotropy of the radicals, the rates of reorientation about the principle axes depend differently on solvent viscosity. This leads to viscosity dependent probabilities for the disproportionation and combination reactions of radical pairs initially formed in unreactive configurations.

4.2. *Qualitative aspects of the collision model. Figure 2* shows two projections A and B of a space filling model of *t*-butyl with its nine hydrogen atoms (white spheres), three methyl carbon atoms (black), and the central carbon atom (striped). A planar configuration of the central carbon atom is assumed, since both the barrier for an umbrella inversion and the average deviation from planarity are small [29]. The axis denoted by ∥ is the symmetry axis of the half-occupied p-orbital. The origin of the rectangular coordinate system formed by the ∥ and the two ⊥ axes coincides with the center of gravity of the radical. Obviously, *t*-butyl resembles an oblate ellipsoid,

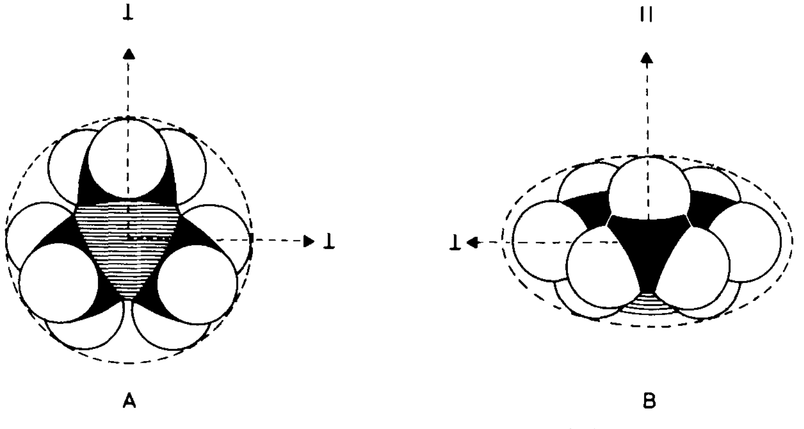

Fig. 2. *Two projections of a space-filling model of* t*-butyl*

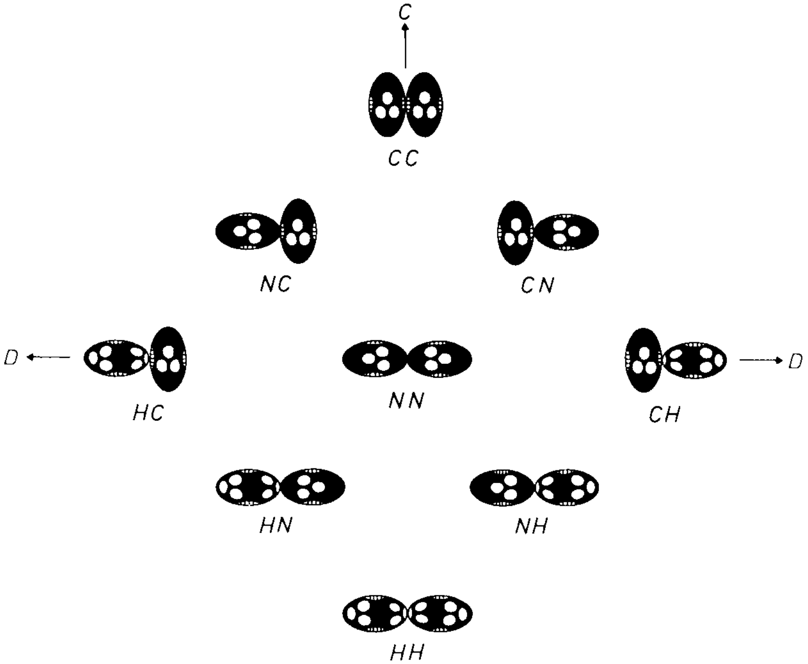

Fig. 3. *Pair configurations of colliding* t-*butyl radicals*

with the steric accessible parts of the central carbon atom at the poles, and the hydrogen atoms in or near to the equatorial plane. This structure of *t*-butyl has two important consequences: Firstly, a reorientation about the ∥ axis affects *only* the hydrogen atoms, and leaves the p-orbital stationary in space. On the other hand, motions about the ⊥ axes reorient both the p-orbital and the hydrogen atoms. Secondly, the reorientational motions of the radical must be anisotropic [30–33], because substantial amounts of fluid are displaced by motions about the ⊥ axes, whereas reorientations about the ∥ axis leave the solvent shell (nearly) unchanged. Further, motions about the ⊥ axes are strongly coupled to the viscosity, whereas those about the ∥ axis are nearly viscosity independent and free.

Henceforth, we assume that both the type of reaction and the reaction probability depend on the relative orientations of the radicals at a collision [3] [34]. *Figure 3* shows nine different pair configurations of colliding *t*-butyl radicals. Here the radicals are approximated by oblate ellipsoids, whose surfaces are divided into three different zones: Firstly, C zones (striped areas) representing the two accessible, reactive surface fractions of the central carbon atom. Secondly, H zones (white spots), standing for the reactive surfaces of the hydrogen atoms. Thirdly, unreactive N zones (black). The various configurations are denoted according to the two zones which are in contact, *e.g.* by CC, NC, HC *etc.* Now, if two free radicals meet, the configurations are populated with probabilities given by the sizes of the zones (see below). Combination reactions occur only from CC, disproportionation reactions only from HC and CH configurations (arrows). All other configurations are unreac-

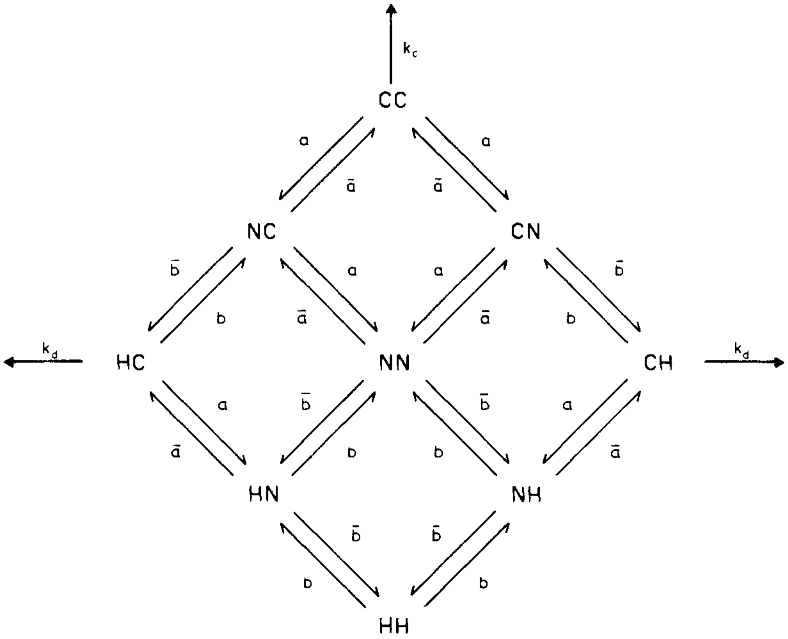

Fig. 4. *Kinetic scheme for the collision model*

tive. In principle they could separate again to give free radicals. We disregard diffusive separation, however, since it is known that all singlet encounters lead to termination in liquids [1] [17]. We rather believe that reorientational motions during the lifetime of the pair [2] [35] [36] induce transitions between the different configurations, transforming the unreactive into reactive ones. As apparent from *Figure 3*, the configuration NC changes to HC by reorientation about the $\parallel$ axis, whereas transitions of NC to CC require motions about a $\perp$ axis. The same holds for transitions of CN to CH or CC, respectively. Since NC and CN are the only unreactive configurations leading directly to CC (*i.e.* by reorientation of one radical), and since reorientations about the $\perp$ axes are more strongly coupled to the viscosity, the probability of combination should decrease with increasing viscosity. This is in agreement with the experimental findings.

4.3. *Quantitative formulation of the collision model.* In the past, effects of reorientational motions on rate constants of bimolecular reactions have found considerable interest [35-41]. Unfortunately, none of the proposed models is directly applicable to our problem, since effects of anisotropic reorientations on product distributions have not yet been considered. However, the formalisms used serve as a guideline. In particular, we follow the quasi-chemical method of *Solc & Stockmayer* [37], and treat the transitions between the different configurations in terms of a simple kinetic scheme *(Fig. 4)*. Herefore, we combine the nine H zones of *Figure 3* to one surface fraction H, and the two C zones to one surface fraction C. With the remaining unreactive fraction N

$$C + H + N = 1 \tag{8}$$

The nine configurations of *Figure 4* are populated with rates $r \cdot X \cdot Y$, where $X, Y = C, H, N$ are the surface fractions and $r = k_t[R\cdot]^2$ is the overall rate of pair formation. Disproportionation and combination products are formed from the configurations HC, CH and CC with rate constants k_d and k_c, respectively. The rate constants a and $\bar{a}$ describe reorientational motions of one radical, changing its relative orientation in the pair from C to N and *vice versa.* Analogously b and $\bar{b}$ denote reorientations exchanging H and N in the pair configurations. The kinetic equations for the populations of the different pairs [XY] are for steady state:

$$[CC]:\ 0 = rC^2 - [CC]\,(k_c + 2a) + [NC]\,\bar{a} + [CN]\,\bar{a} \tag{9a}$$

$$[NC]:\ 0 = rCN - [NC]\,(\bar{a} + a + \bar{b}) + [CC]\,a + [NN]\,\bar{a} + [HC]\,b \tag{9b}$$

$$[CN]:\ 0 = rCN - [CN]\,(\bar{a} + a + \bar{b}) + [CC]\,a + [NN]\,\bar{a} + [CH]\,b \tag{9c}$$

$$[HC]:\ 0 = rHC - [HC]\,(k_d + b + a) + [NC]\,\bar{b} + [HN]\,\bar{a} \tag{9d}$$

$$[CH]:\ 0 = rCH - [CH]\,(k_d + b + a) + [CN]\,\bar{b} + [NH]\,\bar{a} \tag{9e}$$

$$[NN]:\ 0 = rNN - [NN]\ \ (2\bar{a} + 2\bar{b}) + ([CN] + [NC])\,a + ([HN] + [NH])\,b \tag{9f}$$

$$[HN]:\ 0 = rHN - [HN]\,(\bar{a} + b + \bar{b}) + [HC]\,a + [NN]\,\bar{b} + [HH]\,b \tag{9g}$$

$$[NH]:\ 0 = rNH - [NH]\,(\bar{a} + b + \bar{b}) + [CH]\,a + [NN]\,\bar{b} + [HH]\,b \tag{9h}$$

$$[HH]:\ 0 = rHH - [HH]\,2b + ([HN] + [NH]) \cdot \bar{b} \tag{9i}$$

For symmetry reasons [NC] = [CN], [CH] = [HC], and [NH] = [HN]. Further, from the principle of microscopic reversibility [37]:

$$a = \bar{a} \cdot N/C \tag{10a}$$

$$b = \bar{b} \cdot N/H \tag{10b}$$

Using these relations we obtain from (9) for the ratio of disproportionation to combination:

$$\begin{aligned} P_d/P_c &= 2k_d[CH]/k_c[CC] \\ &= \left\{\frac{CH}{N}(2-H) + \frac{2b}{k_c}\frac{H}{C}\left(1+\frac{C}{N}\right) + \frac{b}{a}\frac{H}{C}\left[1 - C^2 + \frac{2C}{N}(1-CH)\right]\right. \\ &\quad \left. + \frac{2b^2}{k_c a}\frac{H}{C}\left(1+\frac{H}{N}\right) + \frac{b^2}{a^2}\frac{H}{C}(1-C^2)\left(1+\frac{H}{N}\right)\right\} : \\ &\quad \left\{\frac{C}{N}(1-H)^2 + \frac{b}{k_d}\left(1+\frac{C}{N}\right) + \frac{b}{a}\left[1 + CH\left(1+\frac{2C}{N}\right)\right] + \frac{b^2}{k_d \cdot a}\left(1+\frac{H}{N}\right)\right. \\ &\quad \left. + \frac{b^2}{a^2}CH\left(1+\frac{H}{N}\right)\right\}. \end{aligned} \tag{11}$$

From this equation, simplified expressions may be obtained: If the reorientations are fast compared to the reactions, *i.e.* a, $b \gg k_d, k_c$, then

$$P_d/P_c = 2k_dH/k_cC \qquad (12)$$

The same relation holds, if no reorientations are possible. On the other hand, if the reorientational motions are strongly anisotropic, and if $b \gg a$:

$$P_d/P_c = (1-C^2)/C^2 \qquad (13)$$

4.4. *Application of the collision model.* In the following, the reorientations of *t*-butyl about the $\parallel$ and the two $\perp$ axes are assumed to be independent, and characterized by the correlation times $\tau_\parallel$ and $\tau_\perp$, respectively. For the rate constants a and b we set *(cf. Fig. 2 and 3).*

$$a = 2\tau_\perp^{-1} \qquad (14)$$

$$b = 2\tau_\perp^{-1} + \tau_\parallel^{-1} \qquad (15)$$

In particular, the rate constant a is independent of $\tau_\parallel$ since the C areas remain stationary on motions about the $\parallel$ axis. As outlined in the preceding section the effects of anisotropy are largest in highly viscous and dense media, for which $\tau_\parallel \ll \tau_\perp$. Since then $b \gg a$, (13) holds. These conditions are certainly fullfilled in solid isobutene at 90 K, where $P_d/P_c \approx 500$ *(Table 1).* Applying (13) to this result gives

$$C^2 \approx 1/500. \qquad (16)$$

In the gas phase, cage effects are absent, and direct transitions between the configurations of colliding pairs are excluded. Then (12) applies. Since disproportionation and combination occur without any classical activation energies, we set rate constants k_d and k_c equal to the collision frequency ν:

$$k_d = k_c = \nu \qquad (17)$$

With (17), any steric factors are included in the concept of the reactive surface fraction. Use of an average gas phase value $P_d/P_c \simeq 2.8$ *(Table 1)*, and (12) and (17) lead to

$$1.4\,C \simeq H \qquad (18)$$

In the following, we assume that the surface fractions C, H and N are independent of the medium. Then, we find from (8), (16) and (18)

$$C = 0.05 \qquad H = 0.06 \qquad N = 0.89$$

i.e. only 5% of the whole surface of *t*-butyl belong to the C area, *ca.* 6% to the H area, and almost 90% to the unreactive surface N. Obviously $C^2, H^2, HC \ll 1$, so that terms in (11) containing these quantities may be neglected. Thus

$$P_d/P_c = \frac{2H\,k_d}{C\,k_c}\left[1 + \frac{k_c(1+b/a) - 2k_d}{2(a+b+k_d)}\right] \qquad (19)$$

Because of the large unreactive surface fraction, and the limited number of collisions in the solvent cage (*ca.* 10–1000, [2] [42]), the reaction probability must be close to unity, if once CC or CH configurations are reached. Therefore, we assume (20) and equation (19) simplifies to (21). Insertion of (14) and (15) gives finally (22).

$$k_d \approx k_c \gg a, b \tag{20}$$

$$P_d/P_c = \frac{H}{C}(1 + b/a) \tag{21}$$

$$P_d/P_c = \frac{H}{C}(2 + \tau_{\perp}/2\tau_{\parallel}) \tag{22}$$

According to [31] [32], the molecular reorientation times obey the relation (23),

$$\tau_{\parallel,\perp} = \tau_c \cdot \kappa_{\parallel,\perp} + \tau_{FR} \tag{23}$$

$$\tau_c = \frac{4\pi r^3 \eta}{3kT} \tag{24}$$

$$\tau_{FR} = 2\pi\,(41/360)\,(\theta/kT)^{1/2} \tag{25}$$

where τ_c is the classical *Debye* reorientation correlation time; τ_{FR} is the free rotor reorientation time of a sphere (25) [43], with θ standing for the moment of inertia. The dimensionless coupling constants $\kappa_{\parallel}$ and $\kappa_{\perp}$ vary from 0 to 1, depending on the shape of the molecule and on the type of friction between solute and solvent. For spheres, $\kappa_{\parallel} = \kappa_{\perp} = \kappa$, with $\kappa = 1$ at 'stick' boundary conditions. If the radius r is large $\tau_{FR} \ll \tau_c$, and thus $\tau = \tau_c$. For real, small molecules τ_c requires a twofold correction: Firstly, a spherical shape is not given in most cases. Secondly, the 'slip' rather than 'stick' boundary condition holds, since in the absence of strong solute-solvent interactions, the first solvent layer does not 'stick' to the solute. For ellipsoids, both corrections are known for different ratios of the semiaxes [33] [44], and $\kappa_{\parallel,\perp}$ of (23) is a product of two factors:

$$\kappa_{\parallel,\perp} = \kappa^{P}_{\parallel,\perp} \cdot \kappa^{HZ}_{\parallel,\perp} \tag{26}$$

The geometrical correction $\kappa^{P}_{\parallel,\perp}$ was computed by *Perrin* [44] for 'stick' boundary conditions. For *t*-butyl, this correction is small, *i.e.* $\tau^{P}_{\parallel}$ and $\tau^{P}_{\perp}$ differ by less than 10%. Hence we assume $\kappa^{P}_{\parallel,\perp} \simeq 1$.

$\kappa^{HZ}_{\parallel,\perp}$ corrects for friction changes from 'stick' to 'slip' conditions, and was computed by *Hu & Zwanzig* [33]. Numerical values of $\kappa^{HZ}_{\parallel,\perp}$ for oblate ellipsoids and various ratios s of the shorter to the longer semiaxis are listed in *Table 4.*

While (23) has been tested for low viscous, neat liquids [31] [32], we doubt that it holds if solute and solvent are strongly different, and if the macroscopic solvent viscosity η is high. In these cases, a correction of the conventional hydrodynamic

Table 4. *'Slip' correction factors κ^{HZ} for oblate ellipsoids as a function of the ratio s of the shorter to the longer semiaxis*[a])

s	κ^{HZ}	s	κ^{HZ}	s	κ^{HZ}
1	0.0	0.65	0.112	0.30	0.572
0.95	0.00169	0.60	0.154	0.25	0.664
0.90	0.00712	0.55	0.203	0.20	0.755
0.85	0.0169	0.50	0.261	0.15	0.842
0.80	0.0316	0.45	0.327	0.10	0.918
0.75	0.0520	0.40	0.402	0.05	0.976
0.70	0.0787	0.35	0.484		

[a]) Taken from [33].

theory from 'stick' to 'slip' boundary conditions is insufficient, as outlined previously [1] for translational diffusion coefficients D_t. Therefore, we replace η in (23) and (24) by the *Stokes-Einstein* equation for 'slip' boundary conditions and use diffusion

$$\eta = kT/4\pi r D_t \qquad (27)$$

coefficients D_t of *t*-butyl estimated *via* the *von Smoluchowski* equation from termination rate constants k_t [1]. Combination of (22), (23), (24) and (27) leads to (28a) with β and γ given by (28b) and (28c).

$$P_d/P_c = 5H/2C + \beta \cdot (D_t + \gamma)^{-1} \qquad (28a)$$

$$\beta = (\kappa_\perp - \kappa_\parallel)\, H \cdot r^2/6C \cdot \tau_{FR} \qquad (28b)$$

$$\gamma = \kappa_\parallel \cdot r^2/3\tau_{FR} \qquad (28c)$$

Since P_d/P_c and D_t are known, the constants $5H/2C$ and β are readily obtained from linear regression calculations, if the term $(D_t+\gamma)^{-1}$ in (28a) is chosen as the independent variable. The constant γ is found by optimizing the correlation coefficient in repeated regressions. The data for D_t and P_d/P_c used in the calculations are listed in *Table 5*. For TMS as the solvent, self-termination rate constants k_t are unknown. Therefore, D_t was calculated following the method of *Spernol & Wirtz* [1] [45], and from viscosity data given by *Vesel* [14]. The analysis then leads to (29 a-c) with an optimum correlation coefficient $r^2 = 0.96$. From (29a) (30) is obtained.

$$5H/2C = 3.63 \qquad (29a)$$

$$\beta = 5.24 \cdot 10^{-5}\,[cm^2 \cdot s^{-1}] \qquad (29b)$$

$$\gamma = 2.4 \cdot 10^{-6}\,[cm^2 \cdot s^{-1}] \qquad (29c)$$

$$1.45\,C = H \qquad (30)$$

which is in excellent agreement with 1.4 $C=H$ estimated above (18). From the ratio of β/γ then

$$\kappa_{\parallel}/\kappa_{\perp}=3.2\cdot 10^{-2} \tag{31}$$

To discuss this result we determine the ratio of the shorter to the longer semiaxis for motions of *t*-butyl around the $\perp$ axis from projection B of *Figure 2* as given in (32a) which yields with *Table 4* (32b).

$$s_{\perp}=0.6 \tag{32a}$$

$$\kappa_{\perp}=0.154 \tag{32b}$$

For ideal ellipsoids and 'slip', rotations about the $\parallel$ axis are inertial, *i.e.* $\kappa_{\parallel}=0$. Now, projection A of *t*-butyl *(Fig. 2)* is not perfectly circular, and its complicated shape cannot be approximated by an ellipsoid. For such cases, *Bauer et al.* [31] suggested the determination of κ from the ratio s of the shortest to the longest dimension perpendicular to the reorientation axis. From the ratio of the height of projection A to the diameter of its dotted circumference we find (33a) and interpolation from *Table 4* yield an estimated value of $\kappa_{\parallel}$:

$$s_{\parallel}\simeq 0.94 \tag{33a}$$

$$\kappa_{\parallel}\simeq 3\cdot 10^{-3}. \tag{33b}$$

From (32b) and (33b) we can obtain:

$$\kappa_{\parallel}/\kappa_{\perp}\simeq 2\cdot 10^{-2} \tag{34}$$

Obviously, the observed value (31) is of the expected order of magnitude.

Finally, combination of (28c) and (29) leads to (35), if the hydrodynamic radius

$$\tau_{FR}=0.54\cdot 10^{-12}\,[s] \tag{35}$$

of *t*-butyl is taken as $r=2.8\cdot 10^{-8}$ cm [1]. (25) and an average temperature of the measurements T=310 K give (36) with the moment of inertia of *t*-butyl

$$\tau_{FR}=0.41\cdot 10^{-12}\,[s] \tag{36}$$

$\theta\simeq 1.4\cdot 10^{-38}$ g · cm^2 estimated from data for isobutane and isobutene [46]. In view of the theoretical and experimental uncertainties, the various agreements are surprisingly good.

With the aid of the fitted parameters, ratios $\tau_{\parallel}/2\tau_{\perp}$ and P_d/P_c are easily calculated for the different solvents and temperatures using (22), (23), (24) and (27). These ratios are also given in *Table 5*, together with ratios of calculated to experimental P_d/P_c. In *Figure 5*, a representative choice of experimental P_d/P_c data is plotted versus $\tau_{\perp}/2\tau_{\parallel}$, showing the predicted linearity (22).

Table 5. *Diffusion coefficients D_t, experimental and calculated ratios P_d/P_c, and ratios $\tau_\perp/2\tau_\parallel$*

Solvent	T [K]	D_t [10^{-6} cm$^2\cdot$s^{-1}]	P_d/P_c (Exp.)	P_d/P_c (Calc.)	Calc./Exp.	$\tau_\perp/2\tau_\parallel$
n-C_8H_{18}	298	31	5.4	5.2	0.96	1.57
	323	43	4.4	4.8	1.09	1.32
	360	63	4.1	4.4	1.07	1.06
n-$C_{10}H_{22}$	298	26	5.7	5.5	0.96	1.79
	323	37	4.6	4.95	1.08	1.41
	360	56	4.3	4.5	1.05	1.11
n-$C_{12}H_{26}$	298	19.3	5.9	6.1	1.03	2.17
	323	28	4.9	5.4	1.09	1.69
	342	35	4.7	5.1	1.09	1.48
	360	43	4.5	4.8	1.06	1.29
n-$C_{14}H_{30}$	298	15.4	6.4	6.6	1.03	2.53
	323	24	5.1	5.6	1.10	1.88
	360	40	4.7	4.9	1.04	1.35
n-$C_{16}H_{34}$	298	13.6	6.9	6.9	1.0	2.77
	323	22	5.4	5.8	1.07	1.99
	342	30	5.0	5.2	1.05	1.60
	360	39	5.0	4.9	0.98	1.35
OMCTS[a])	290	14.4	6.8	6.7	0.99	2.63
	342	39	4.4	4.9	1.12	1.38
	360	51	4.2	4.6	1.10	1.17
TMS[a])	180	6.0	8.5	9.9	1.16	4.8
	221	18.6	6.2	6.1	0.99	2.2
	252	35	5.3	5.1	0.96	1.48
	298	71	4.1	4.3	1.05	0.99
t-ButOH/ Pin 1:2[a])	265	0.28	23.5	23.2	0.99	14.0
	267	0.35	22.0	22.7	1.03	13.6
	271	0.48	21.0	21.8	1.04	13.0
	276	0.71	19.1	20.4	1.07	12.1
	287	1.6	13.3	16.7	1.25	9.5
	298	3.2	10.3	12.9	1.26	6.9
	322	9.3	8.3	8.1	0.98	3.6
	342	17.8	6.9	6.2	0.90	2.3
	361	29	5.5	5.3	0.97	1.66
3-Methyl-3-pentanol (3 MP)	245	1.2	23.5	18.2	0.77	10.5
	250	1.6	19.0	16.8	0.89	9.6
	255	2.1	16.2	15.3	0.94	8.5
	262	2.9	13.7	13.6	0.99	7.4
	281	6.6	9.9	9.4	0.95	4.5
	298	12.3	7.5	7.2	0.96	2.9
	319	25	6.1	5.5	0.91	1.82
	328	34	5.7	5.1	0.89	1.48
	343	49	5.4	4.7	0.87	1.22
	352	58	5.0	4.5	0.90	1.10
	356	62	5.0	4.4	0.89	1.06
	361	68	4.8	4.4	0.91	1.02
	371	79	4.7	4.3	0.91	0.94

[a]) For abbreviations see *Table 1* and *2*.

5. *Conclusions and comments on the collision model.* Apparently, the collision model describes the experimental P_d/P_c data essentially within experimental error. These findings, and the good agreement of the fitted values of C/H, $\kappa_\parallel/\kappa_\perp$ and τ_{FR} with independent estimates lead us to believe that anisotropic reorientations of the radicals in the solvent cage actually determine the temperature and medium dependence of P_d/P_c for *t*-butyl. Further, the values of $\kappa_\parallel/\kappa_\perp$ and τ_{FR} confirm the assumption that *t*-butyl reorients in a similar fashion as other small non-associating molecules [31] [32]. This excludes strong radical-solvent [47] or radical-radical complexes [48], and agrees with similar findings for translational diffusion [1]. The good agreement of the ratios C/H in the gas and in the liquid phase strongly supports the idea that the kinetic behaviour of *t*-butyl is very similar in both phases, except for cage effects. With (16), (18) and (32) the reactive surface fraction of one single hydrogen atom H/9 is less than 1% of the total surface of *t*-butyl, and only *ca.* 16% of the C-surface fraction. This probably reflects the relatively high orientational requirements for the hydrogen transfer in the disproportionation reaction, *i.e.* mainly collisions collinear to the C–H bond lead to reaction [49]. Now, if this is true, internal rotations of the methyl groups are likely to influence the probability for disproportionation reactions, and since methyl rotations are activated processes [50], they could also influence the temperature dependence of P_d/P_c. In the determination of $\tau_\perp/2\tau_\parallel$ used here, any methyl rotations are automatically included in $\tau_\parallel$. Therefore, the ratios $\tau_\perp/2\tau_\parallel$ of *Figure 5* and *Table 5* represent an upper limit for the actual anisotropy of the reorientations of the whole molecule. However, the effects of methyl rotations must be comparatively small, since the values of $\kappa_\parallel$ and τ_{FR} are

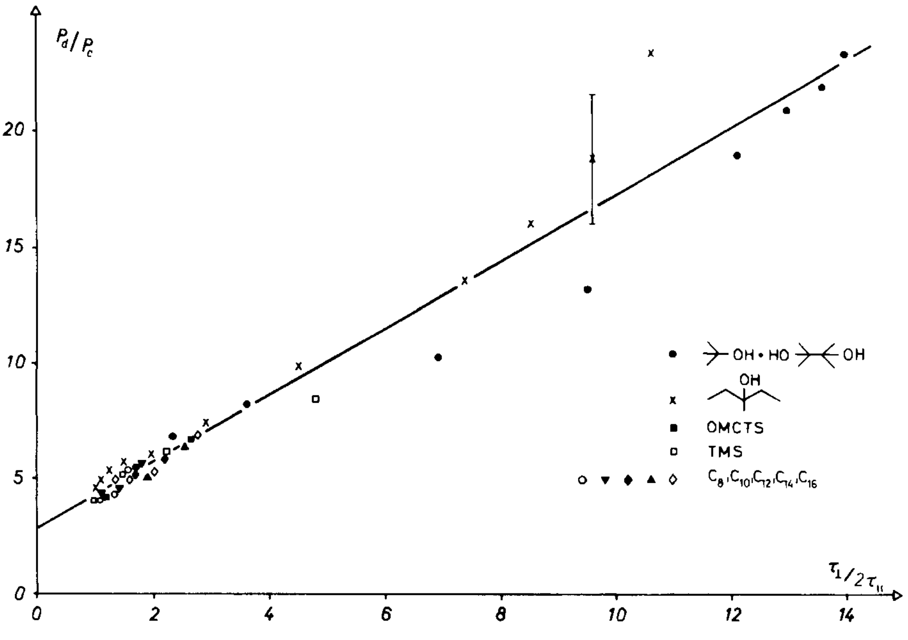

Fig. 5. *Predicted linear relation (22) between P_d/P_c of* t-*butyl in liquids and* $\tau_\perp/2\tau_\parallel$ (for data see *Table 5*)

in good accord with the structure of the whole molecule. Finally, limiting values of P_d/P_c derived from (22) or (30) for extremely fast or slow diffusion should be considered with some caution, because of the assumptions inherent in (14), (15) and (22-25). Clearly, (14) and (15) do not extrapolate correctly for the isotropic case ($\tau_{\parallel} = \tau_{\perp}$; a=b), which is reached if diffusion is very fast. On the other hand, in extremely viscous media the effects of the partner radicals on reorientation cannot be ignored, and it is doubtful whether the rotation- translation coupling remains constant (s. (24) and (29)). Again, the required corrections seem of minor importance here. We conclude from the above findings, and from the diffusion controlled termination reaction [1], that the entire kinetics of self-reacting *t*-butyl radicals in liquids are governed by transport processes, and may be predicted, if the pertinent transport data are known.

As pointed out previously, the self-termination reactions of many other alkyl radicals are also diffusion controlled. This raises the question whether our collision model correctly describes P_d/P_c of other alkyl radicals also. For ethyl radicals, P_d/P_c is well known [3] [11] [21-23] [51] [52]. In alkane solvents, *i.e.* pentane, decalin [11] or isooctane [22] [23] it is equal to the temperature independent gas phase value of *ca.* 0.15 [51], and it increases by somewhat less than a factor of two if determined in viscous ethylene glycol [22], or if an external pressure of up to 600 MPa is applied to the solvent [23]. However, for − 181° in liquid methane, *Gillis* [52] reported $P_d/P_c = 1$ for C_2HD_4 radicals. This result disagrees with the value $P_d/P_c = 0.35$ given by *Dixon et al.* [21] for ethyl in methane at − 184°. Despite the considerable experimental uncertainties, P_d/P_c in liquids seems to increase slightly with pressure and decreasing temperature, or simply with increasing microscopic viscosity. To judge the effects of reorientational motions on P_d/P_c, we draw an orthogonal axis system through the center of gravity of ethyl, with one axis lying in the carbon-carbon bond. It can then be seen that the β-hydrogen atoms and the *p*-orbital reorient in similar fashion on motions about any axis. Therefore, the rate constants a and b of *Figure 4* should be roughly equal, *i.e.* reorientations of the whole molecule are unimportant for P_d/P_c. Hence, we expect P_d/P_c rather independent of the medium. This agrees qualitatively with experiment. The weak increase of P_d/P_c with microscopic viscosity could be due to independent rotations of the methylene and of the methyl group about the carbon-carbon bond, with the methylene group somewhat stronger coupled to the medium.

When a methyl group of *t*-butyl is replaced by a hydroxyl group, 1-hydroxy-1-methylethyl results. Since the weight and size of OH and CH_3 are similar, in a first approximation a similar viscosity dependence of P_d/P_c for 1-hydroxy-1-methylethyl to *t*-butyl is expected. Indeed, *Henne* [53] found for 1-hydroxy-1-methylethyl $P_d/P_c = 4.4$ for 25°, $\eta \simeq 0.3$ mPa · s, and $P_d/P_c = 19$ for −70°, $\eta \simeq 5$ mPa · s. It should be noted, however, that slight deviations from the 'slip' boundary condition are expected for molecules bearing a single hydrogen bonding group [31] [54].

As mentioned in section 3, the yields of pivalaldehyde from reaction (3) of *t*-butyl with pivaloyl increase markedly with solvent viscosity *(Table 3)*. This trend could be due to cage effects. However, only a small fraction of geminate radical pairs is formed in the singlet state [12]. We rather presume the major reason to be viscosity dependence of the disproportionation/combination ratio P_d^x/P_c^x of *t*-butyl and pivaloyl. Indeed, for TMS as the solvent it is known [14] that P_d^x/P_c^x increases continuously from 0.4 at 22° to 3 at −93°, and in benzene $P_d^x/P_c^x = 1$ near room temperature [12]. These values and the increased formation of pivalaldehyde strongly point to a similar viscosity dependence of P_d^x/P_c^x as observed for self-reacting *t*-butyl or 1-hydroxy-1-methylethyl.

To conclude, the collision model agrees qualitatively with many experimental data, but further tests are clearly needed. Therefore, we suggest checking the following prediction: In isobutyl radicals the positions of the H and of the C zone are exchanged with respect to *t*-butyl. Hence, the viscosity dependence of P_d/P_c for isobutyl should be opposite to that of *t*-butyl.

We thank Mrs. *I. Verhoolen* for valuable help with the product analysis, and Dr. *P. W. Percival* for critically reading the manuscript. This work was supported by the *Swiss National Foundation for Scientific Research.*

REFERENCES

[1] *H. Schuh & H. Fischer,* Helv. *61,* 2130 (1978).

[2] a) *T. Koenig & H. Fischer* in 'Free Radicals', ed. J.K. Kochi, Wiley, New York, Vol. I, p. 157ff 1973; b) *J.P. Lorand* in 'Progress in Inorganic Chemistry', ed. J.O. Edwards & S.J. Lippard, Wiley, New York, Vol. 17, pt. 2, p. 207ff 1972.

[3] *M.J. Gibian & R.C. Corley,* Chem. Rev. *73,* 441 (1973).

[4] *D.G.L. James & R.D. Suart,* Trans. Faraday Soc. *65,* 175 (1969).

[5] *W.E. Falconer & W.A. Sunder,* Int. J. chem. Kinetics *3,* 523 (1971).

[6] *J.H. Georgakakos, B.S. Rabinovitch & C.W. Larson,* Int. J. chem. Kinetics *3,* 535 (1971).

[7] *J.A. Garcia Dominguez, J.A. Kerr & A.F. Trotman-Dickenson,* J. chem. Soc. *1962,* 3357.

[8] *D.A. Parkes & C.P. Quinn,* J. chem. Soc. Faraday Trans. I *72,* 1952 (1976).

[9] *K.Y. Choo, P.C. Beadle, L. Piszkiewicz & D.M. Golden,* Int. J. chem. Kinetics *8,* 45 (1976).

[10] *S.F. Nelson & P.D. Bartlett,* J. Amer. chem. Soc. *88,* 137 (1966).

[11] *R.A. Sheldon & J.K. Kochi,* ibidem *92,* 4395 (1970).

[12] *B. Blank, A. Henne & H. Fischer,* Helv. *57,* 920 (1974).

[13] *D. Griller & K.U. Ingold,* J. Amer. chem. Soc. *97,* 1813 (1975).

[14] *P. Vesel,* diploma thesis, University of Zürich 1975.

[15] *H. Schuh & H. Fischer,* Int. J. chem. Kinetics *8,* 341 (1976).

[16] *R.D. Kelley, R. Klein & M.D. Scheer,* J. phys. Chemistry *74,* 4301 (1970).

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

[18] *H. Schuh, E.J. Hamilton Jr., H. Paul & H. Fischer,* Helv. *57,* 2011 (1974).

[19] *H.D. Beckhaus & C. Rüchardt,* Chem. Ber. *110,* 878 (1977).

[20] *J.N. Bradley,* J. chem. Physics *35,* 748 (1961).

[21] *P.S. Dixon, A.P. Stefani & M. Szwarc,* J. Amer. chem. Soc. *85,* 2551 (1963).

[22] *A.P. Stefani,* ibidem *90,* 1694 (1968).

[23] a) *C. Backman,* Ph. D. Thesis, University of Uppsala 1976; b) *C. Backman, S. Claesson & M. Szwarc,* Trans. Faraday Soc. *66,* 3061 (1970).

[24] *R.C. Neuman, Jr.,* J. org. Chemistry *37,* 495 (1972).

[25] *A.F.M. Barton,* J. chem. Educ. *48,* 156 (1971).

[26] *N. Nodelman & N.C. Martin,* J. Amer. chem. Soc. *98,* 6597 (1976).

[27] *I.A. Wiche & E.B. Bagley,* Amer. Inst. chem. Eng. (AIChE)-J. *13,* 836 (1967).

[28] *G. Allen, G. Gee & G.J. Wilson,* Polymer *1*, 456 (1960).

[29] *J.B. Lisle, L.F. Williams & D.E. Wood,* J. Amer. chem. Soc. *98*, 227 (1976); *P.J. Krusic & P. Meakin,* ibidem *98*, 228 (1976); *L. Bonazzola, N. Leray & J. Roncin,* ibidem *99*, 8348 (1977).

[30] *J. Hwang, D. Kivelson & W. Plachy,* J. chem. Physics *58*, 1753 (1973).

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

[32] *M. Fury & J. Jonas,* J. chem. Physics *65*, 2206 (1976).

[33] *C. Hu & R. Zwanzig,* ibidem *60*, 4354 (1974).

[34] *K.J. Skinner, R.J. Blaskiewicz & J.M. McBride,* Israel J. Chemistry *10*, 457 (1972).

[35] *T. Koenig & J.M. Owens,* J. Amer. chem. Soc. *96*, 4052 (1974), and references cited therein.

[36] *J.F. Garst,* ibidem *97*, 5062 (1975).

[37] *K. Solc & W.H. Stockmayer,* Int. J. chem. Kinetics *5*, 733 (1973).

[38] *E.L. Simmons,* Z. physik. Chem. N.F. *96*, 47 (1975).

[39] *J.M. Schurr & K.S. Schmitz,* J. phys. Chemistry *80*, 1934 (1976).

[40] *E.T. Denisov,* Bull. Acad. Sciences USSR, Div. Chem. Science *25*, 41 (1976) (Izv. Akad. Nauk SSR, Ser. Chim. 51, *1976*); *A.P. Griva, L.N. Denisova & E.T. Denisov,* Doklady phys. Chemistry *232*, 213 (1977) (Doklady Akad. Nauk SSR *232*, 1343 (1977)).

[41] *A.I. Burshtein & B.I. Yakobson,* Chem. Physics *28*, 415 (1978).

[42] *I.D. Clark & R.P. Wayne* in 'Comprehensive Chemical Kinetics', eds. C.H. Bamford & C.F.H. Tipper, Elsevier, Amsterdam, Vol. 2, p. 302ff 1969.

[43] *F.J. Bartoli & T.A. Litovitz,* J. chem. Physics *56*, 404; 413 (1972).

[44] *F. Perrin,* J. Phys. Radium *5*, 497 (1934).

[45] *A. Spernol & K. Wirtz,* Z. Naturforschung *8a*, 522 (1963).

[46] Landolt-Börnstein, New Series, ed. K.H. Hellwege & B. Starck, Springer Verlag Berlin, Vol. II/4, p. *39*, 110, 1967.

[47] *R.D. Burkhart & R.J. Wong,* J. Amer. chem. Soc. *95*, 7203 (1973).

[48] *H. Langhals & H. Fischer,* Chem. Ber. *111*, 543 (1978).

[49] *R.N. Porter & M. Karplus,* J. chem. Physics *40*, 1105 (1964); *A.R. Miller,* J. Amer. chem. Soc. *100*, 1984 (1978), and references cited therein.

[50] *S. Berger, F.R. Kreissl, D.M. Grant & J.D. Roberts,* J. Amer. chem. Soc. *97*, 1805 (1975).

[51] *D.G. Hooper, M. Simon & M.H. Back,* Canad. J. Chemistry *53*, 1237 (1975).

[52] *H.A. Gillis,* ibidem *49*, 2861 (1971).

[53] *A. Henne,* Ph. D. Thesis, University of Zürich 1975.

[54] *W.W. Mantulin & G. Weber,* J. chem. Physics *66*, 4092 (1977).