

Figure 5. Effects of HBr addition on the spatial distributions of labile intermediates in a free-burning methanol-air flame. The full lines and the dashed lines denote the flame without and with addition of 5 vol % HBr aqueous solution (47.6%) into methanol.

Figure 5 shows the concentration profiles for a flame of methanol containing 5 vol % of HBr and with $\phi = 0.71$ (composition in the gas phase: CH₃OH, 8.7%; HBr, 0.12%; H₂O, 0.61%; O_2 , 19.0%; and N_2 , 71.7%). The concentration profiles in a pure (uninhibited) methanol-air flame of $\phi = 0.68$ are for comparison also shown in Figure 5. It should be noted that addition of 5 vol % H₂O to a methanol-air flame was not enough to alter the concentration profiles.

Distinct features of the HBr addition are decreases in the concentrations of H, O, and OH and a shortening of the width of their distribution zones. This decrease in concentration is most prominent for the H atoms, where the maximum concentration is reduced by more than 2 orders of magnitude. The prominent decrease in the H atom concentration agrees qualitatively with the proposed model for flame inhibition by HBr in methane and methanol combustions,¹⁸ where the inhibition is mostly the result

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of the combined effects of the following reactions:

$$H + HBr \rightarrow H_2 + Br \tag{5}$$

$$H + Br_2 \rightarrow HBr + Br \tag{6}$$

$$Br + Br + M \to Br_2 + M \tag{7}$$

Br atoms exist in a high concentration in the whole flame region, as can be seen in Figure 5. About 70% of the bromine added exists in the atomic form. These observations are in good agreement with the results obtained from model calculations.¹⁸ The observed flame shrinkage is probably a result of the reduction of H atoms in the inner flame region which causes an insufficient generation of O atoms and OH radicals by reaction 2 in the outer flame region, together with scavenging reactions like $O + HBr \rightarrow OH$ + Br and OH + HBr \rightarrow H₂O + Br.

Conclusion. The concentration profiles of H, O, and OH (and Br for the HBr-inhibited flame) have been observed for the premixed methanol-air flames burning freely under atmospheric environment. Although the spatial resolution of the probe-sampling technique is not high enough to examine in detail the profiles in the narrow inner flame region, the present probe sampling-EPR detection method combined with the free-burning flame has been shown to be convenient and useful to study the chemical modification of the flame by adding solutes in methanol fuel. The addition of H₂O affects mainly the reactions in the inner flame region, resulting in the enhanced generation of OH and the reduction of O, whereas the addition of HBr reduces the concentrations of all the H, O, and OH intermediates in the whole region of the flame. The present experimental results along with further extension along the same lines will serve as a countercheck of and as a clue for modeling of complex combustion chemistry in actual flames.

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Absolute Rate Constants for the Self-Termination of the Isopropyl Radical and for the Decarbonylation of the 2-Methylpropanoyl Radical

Juraj Lipscher and Hanns Fischer*

Physikalisch-Chemisches Institut der Universität, CH-8057 Zürich, Switzerland (Received: August 23, 1983)

Rate constants for the self-termination of isopropyl radicals $((CH_3)_2CH)$ generated by photolysis of diisopropyl ketone ((CH₃)₂CHCOCH(CH₃)₂) in various liquids have been determined by kinetic electron spin resonance and are found to be diffusion controlled. The ratio of disproportionation to combination is nearly independent of temperature and solvent viscosity as suggested by the radical's structure. In tetraethoxysilane the rate constant for the decarbonylation of the 2-methylpropanoyl radical ((CH₃)₂CHCO) can be represented by log (k/s^{-1}) = (14.0 ± 0.5) - (54.5 ± 2.0)/2.3RT kJ/mol.

Introduction

In recent years the effects of diffusion on the self-termination reactions of several small sterically unhindered carbon radicals in liquids have been studied extensively by us and others.¹⁻⁹

Generally, it was found that the rate constants are well described by predictive equations for control by translational diffusion and spin statistics.^{10,11} For *tert*-butyl and isopropylol radicals the ratio

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of disproportionation to combination increased strongly with solvent viscosity, and this was explained by anisotropic reorientational diffusion of the radicals during encounters.^{1,3,12} To test the validity of the previous concepts of analysis with another system we have now studied the product distribution and the kinetics of the self-reaction of isopropyl radicals generated by photolysis of diisopropyl ketone in various liquids.¹³ In the course of this work rate constants for the decarbonylation of the 2-methylpropanoyl radical were also obtained which extend the utility of such reactions as internal free radical "clocks".14

Experimental Section

The techniques used for the determinations of photolysis product yields, radical concentrations, and rate constants by steady-state and time-resolved electron spin resonance and for measurements of diffusion coefficients have been described in detail previously.^{3,5} The solvents used in this work were purified by column chromatography or distillation prior to use.

Results and Discussion

Photolysis of 7.1 \times 10⁻² M solutions of diisopropyl ketone (n π^* transition region) in various solvents to about 4% conversion leads to the products given in Table I. In agreement with previous work¹⁵⁻¹⁷ they suggest the reactions

$$(CH_3)_2 CHCOCH(CH_3)_2 \xrightarrow{h\nu} (CH_3)_2 CHCO + (CH_3)_2 \dot{C}H$$
(1)

$$(CH_3)_2 CHCO \rightarrow (CH_3)_2 CH + CO$$
(2)

$$(CH_3)_2CH \rightarrow CH_3CH_2CH_3 + CH_2 = CHCH_3 \qquad (3)$$

$$2(CH_3)_2\dot{C}H \rightarrow (CH_3)_2CHCH(CH_3)_2 \qquad (4)$$
$$(CH_3)_2CH\dot{C}O + (CH_3)_2\dot{C}H \rightarrow$$

 $(CH_3)_2$ CHCHO + CH₂=CHCH₃ (5)

$$(CH_3)_2 CHCO + (CH_3)_2 CH \rightarrow (CH_3)_2 CHCOCH(CH_3)_2 \quad (6)$$

$$2(CH_3)_3CH\dot{C}O \rightarrow (CH_3)_3CHCOCOCH(CH_3)_3$$
 (7)

with (1)-(4) dominating. The yield of isobutyraldehyde decreases strongly with increasing temperature which points to a large activation energy for the decarbonylation (reaction 2). Above $T \ge 40$ °C decarbonylation is fast compared to termination reactions 3-7, and the photolysis provides a clean source for isopropyl radicals as needed for kinetic electron spin resonance investigations. However, a significant excess of propane over propene found at elevated temperatures and the deviation of the quantity α = $[C_3H_8]/([C_3H_6] - [(CH_3)_2CHCHO])$ from the expected value of one (Table I) indicates an additional reaction for propane formation. Evidence described below shows that this is a hydrogen abstraction reaction by isopropyl radicals from the parent ketone, which is also known to occur in the gas phase.¹⁵ The last column of Table I gives ratios of disproportionation to combination calculated from the yields of propene, aldehyde, and coupling product. They decrease slightly with increasing temperature and do not depend grossly on the solvent. Our values agree well with the previous result of $P_d/P_c = 1.2$ at 30 °C in decalin¹⁸ and are somewhat smaller than $\ddot{P}_{\rm d}/\dot{P}_{\rm c} = 1.63$ for perdeuterated isopropyl at room temperature extrapolated from low temperature measurements¹⁹ and larger than the gas-phase values²⁰ of $P_d/P_c =$

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Figure 1. Concentrations of CH₃CHCH₃ during steady-state photolysis of diisopropyl ketone vs. temperature (initial ketone concentration, 7.1 \times 10⁻² M; average conversion, \approx 5%, solvent, tetraethoxysilane).

0.7. They will be discussed later.

Reactions 1-7 are strongly supported by ESR spectra taken during steady-state photolysis of diisopropyl ketone. For $T \ge 20$ °C only isopropyl is observed, whereas both isopropyl and 2methylpropanoyl (broad singlet at $g = 2.0007^{17}$) are found at lower temperatures. Figure 1 shows the steady-state concentration of isopropyl in arbitrary units as a function of temperature. For -10 $\leq T \leq 35$ °C the general decrease due to increasing termination rates (reactions 3-7) is intersected by an increase attributable to the activated decarbonylation (reaction 2). A similar behavior was observed previously for analogous cases of decarbonylation.^{2,21}

Since, obviously, decarbonylation is fast compared to the terminations only for $T \ge 35$ °C, self-termination rate constants $2k_t$ = $2(k_3 + k_4)$ were measured only at higher temperatures. Figure 2 shows a kinetic trace taken with the K(CH) = 1/2, M(CH) = $\frac{1}{2}$, $K(CH_3) = 1$, $M(CH_3) = +1$ transition of the fully resolved second-order spectrum of isopropyl. The smooth line overlying the experimental trace in the light-off period is a least-squares fit to the rate law valid for a second-order decay perturbed to a minor extent by a concurring pseudo-first-order reaction²²

$$[\mathbf{R} \cdot] = [\mathbf{R} \cdot]_0 \frac{e^{-t/\tau_1}}{1 + \frac{1}{2} \left[1 + \left(1 + \frac{4\tau_2}{\tau_1} \right)^{1/2} \right] \frac{t}{\tau_2}}$$
(8)

Here, $[\mathbf{R} \cdot]_0$ is the steady-state concentration at the end of the light-on period, τ_2 is the second-order lifetime $(2k_t[\mathbf{R}\cdot]_0)^{-1/2}$, and τ_1 is the pseudo-first-order lifetime. A nonnegligible contribution of the pseudo-first-order reaction was found for all systems studied.¹³ It increased with increasing temperature. More significantly, τ_1^{-1} increased linearly with increasing concentration of ketone. Therefore, we attribute the pseudo-first-order term to the reaction of the isopropyl radical with diisopropyl ketone by hydrogen atom abstraction. This also explains the excess

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		$(CH_3)CHCH (CH_3)_2$ -					
solvent	<i>T</i> , °C	C ₃ H ₈	C_3H_6	(CH ₃) ₂	CHCHO	α^b	$P_{\rm d}/P_{\rm c}{}^c$
n-heptane	0	1.02	1.19	0.76	0.32	1.17	1.15
	10	1.25	1.30	0.96	0.23	1.17	1.12
	20	1.49	1.40	1.18	0.16	1.20	1.05
	40	1.56	1.38	1.30	0.11	1.23	0.98
	50	1.67	1.38	1.36	0.04	1.25	0.99
	60	1.60	1.37	1.41	0.03	1.19	0.95
	70	1.82	1.44	1.55	0.03	1.29	0.91
	80	1.52	1.09	1.18	0.02	1.42	0.91
	90	1.67	1.17	1.28		1.43	0.91
n-dodecane	0	0.98	1.07	0.59	0.29	1.26	1.32
	10	1.14	1.11	0.74	0.22	1.28	1.20
	20	1.27	1.14	0.86	0.14	1.27	1.16
	30	1.34	1.16	0.94	0.11	1.28	1.12
	40	1.41	1.16	0.99	0.09	1.32	1.08
	50	1.62	1.22	1.08		1.33	1.13
	60	1.64	1.18	1.09		1.39	1.08
	70	1.66	1.13	1.08		1.47	1.05
	80	1.54	1.00	0.93		1.54	1.08
3-methyl- pentan-3-ol	0	1.07	1.37	0.75	0.41	1.11	1.28
-	10	1.10	1.23	0.81	0.27	1.15	1.19
	20	1.38	1.42	1.03	0.22	1.15	1.17
	30	1.22	1.19	1.03	0.15	1.17	1.01
	40	1.54	1.44	1.30	0.10	1.15	1.03
	50	1.42	1.28	1.18	0.07	1.17	1.03
	60	1.76	1.54	1.50	0.07	1.20	0.98
	70	1.41	1.18	1.23	0.04	1.23	0.93
	80	1.71	1.41	1.50	0.02	1.23	0.93
	90	1.50	1.15	1.23	0.02	1.33	0.92

^aGlc analyses of two-three runs, errors ± 0.05 mM, rate of radical generation $I = (3.5 \pm 0.5) \times 10^{-4}$ M s⁻¹. ^b $\alpha = [C_3H_8]/([C_3H_6] - [(CH_3)_2CHCHO])$. ^c $P_d/P_c = ([C_3H_6] - [(CH_3)_2CHCHO])/[(CH_3)_2CHCH(CH_3)_2]$.



Figure 2. Concentration of CH₃CHCH₃ vs. time during intermittent photolysis of diisopropyl ketone in *n*-hexadecane (initial ketone concentration, 7.1 × 10⁻² M; average conversion, $\simeq 5\%$; least-squares fit parameters τ_1 , τ_2 given for this run. Standard deviations for six runs are 5% for τ_2 and about 15% for τ_1).

formation of propane (vide supra). Analysis of the temperature dependence of τ_1 leads to the Arrhenius parameters log $(A/M^{-1} s^{-1}) = 6.9 \pm 0.5$ and $E_a = (18.8 \pm 5.4)$ kJ/mol as averages for the different solvents used.¹³

Self-termination rate constants for isopropyl are collected in Table II. They are averages of six individual measurements and believed to be accurate to $\pm 25\%$. From $2k_t$ and $[R \cdot]_0$ the rate of radical generation was calculated for each run. It varied only slightly with solvent and temperature¹³ ($I = (7.9 \pm 0.3) \times 10^{-4}$ M s⁻¹ for tetraethoxysilane). Diffusion coefficients needed for the analysis were measured for propane and propene by the chromatographic broadening technique⁵ and are also given in Table II. The table further shows diffusion coefficients calculated for propane from the solution viscosities and the molecular volumes via the predictive treatments of Stokes-Einstein (D^{SE}) , Spernol and Wirtz²³ (D^{SW}) , and Lusis and Ratcliff²⁴ (D^{LR}) . As found previously for isobutane¹ the Stokes-Einstein treatment grossly

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FABLE II: Rate Constants f	or the Self-	Termination of	Isopropyl Rad	licals and]	Diffusion	Coefficients o	f Propane and	l Proper
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solvent	<i>T</i> , °C	$2 \times 10^9 k_t^b$	10 ⁻⁵ D _{C₃H₈} ^c	$10^{-5} D_{C_3 H_6}^{c}$	D _{C3H8}	D _{C₃H₈}	$D_{C_3H_8}^{LR}$	
n-heptane ^a	40	8.7	5.4	6.1	2.4	6.0	6.0	
-	50	9.9	6.0	6.6	2.7	6.8	6.9	
	60	9.9	6.6	7.3	3.0	7.5	7.8	
	70	10.8	7.2	8.0	3.4	8.3	8.8	
	80	11.1	7.8	8.7	3.7	9.2	9.9	
n-hexadecane ^a	40	3.1	1.5	1.8	0.3	1.5	1.2	
	50	3.7	1.8	2.1	0.4	1.8	1.5	
	60	4.0	2.1	2.5	0.5	2.2	1.8	
	70	4.6	2.4	2.8	0.6	2.6	2.2	
	80	5.2	2.7	3.1	0.7	3.1	2.6	
tetraethoxy- silane ^a	40	6.2	3.5	3.5	1.4	4.5	4.4	
	50	7.1	3.9	3.9	1.6	5.1	5.1	
	60	8.0	4.3	4,4	1.8	5.7	5.7	
	70	8.2	4.8	4.8	2.1	6.4.	6.5	
	80	8.0	5.2	5.2	2.3	7.1	7.3	
3-methyl- pentane-3-ol ^a	40	3.3	1.5	1.7	0.3	1.0	0.8	
-	50	4.5	1.9	2.0	0.5	1.5	1.3	
	60	5.2	2.3	2.5	0.8	2.2	2.0	
	70	5.4	2.8	2.9	1.2	3.2	3.1	
	80	5.9	3.3	3.3	1.8	4.6	4.5	

^aSolutions contained 7.1 × 10⁻² M diisopropyl ketone. ^bM⁻¹ s⁻¹; statistical errors of experimental data $\leq 10\%$ (six runs). ^ccm² s⁻¹; statistical errors of experimental data $\leq 4\%$ (four-six runs).

underestimates D, whereas the other treatments yield satisfactory estimates. To test the self-termination constants for diffusion control we calculated $2k_t$ from the Smoluchowski equation¹⁰

$$2k_t^{s} = 8\pi (1000)^{-1} N_l D\rho\sigma \tag{9}$$

the Noyes' modification¹⁰

$$2k_{t} = 2k_{t}^{s}(1 + 2k_{t}^{s}/2\sigma k_{0})^{-1}$$
(10)

and the extension suggested by Sitarski¹¹

$$2k_{t} = 2k_{t}^{s}[0.2\alpha^{2}K + \alpha(2 - \alpha)] \times \\ [0.06\pi(2 - \alpha)\alpha K^{2} + (0.68\alpha^{2} + 0.1\pi(2 - \alpha)^{2})K + \alpha(2 - \alpha)]^{-1}$$
(11)

Here D is the diffusion coefficient of the radical, ρ the reaction distance, σ the spin statistical factor, k_0 the radiation boundary constant, $0 \le \alpha \le 1$ a reactivity parameter, and $K = 10D\rho^{-1}$. $(M/2\pi RT)^{1/2}$ the effective Knudsen number. As in previous work¹⁻⁶ D is approximated by the diffusion coefficient of a parent molecule, and the average of $D_{C_3H_6}$ and $D_{C_3H_6}$ (Table II) was used. The spin statistical factor was taken as 1/4, and $\rho = 5.2 \times 10^{-8}$ cm was obtained from usual estimations.¹⁻⁶ Figure 3 represents $2k_1$ plotted vs. diffusion coefficient. The straight line 1 is obtained from eq 9. Curve 2 follows from eq 11 with $\alpha = 1$ and an average temperature of 60 °C. Curve 3 is a least-squares fit of eq 10 to the data and corresponds to $2\sigma k_0 = 4.3 \times 10^{10}$ M⁻¹ s⁻¹. The agreement between experimental and predicted rate constants is very satisfactory and confirms the validity of the predictive procedures previously introduced.¹⁻⁶

Knowledge of the rate constants for self-termination enables a determination of the kinetics of the decarbonylation reaction (reaction 2) in tetraethoxyethane from the data of Figure 1. Since isopropyl and 2-methylpropanoyl radicals have similar sizes and since the termination reactions of isopropyl radicals are diffusion controlled it seems very likely that all terminations (reactions 3-7) occur with very similar rate constants. Then, taking $2(k_3 + k_4)$ = $(k_5 + k_6) = 2k_7 = 2k_1$ and neglecting side reactions one derives from reactions 1-7 for the steady-state concentration of isopropyl³

$$[\mathbf{R} \cdot] = (I/k_t)^{1/2} \frac{1 + (Ik_t)^{1/2}/k_2}{1 + 2(Ik_t)^{1/2}/k_2}$$
(12)

where I is rate of radical generation (reaction 1) and k_2 is the rate constant of decarbonylation (reaction 2). The solid curve



Figure 3. Self-termination rate constants of isopropyl in *n*-heptane (Δ) , *n*-hexadecane (\Box) , tetraethoxysilane (\bullet) , and 3-methylpentan-3-ol (O). For curves 1-3, see text.

drawn in Figure 1 is a least-squares fit of eq 12 to the data and was obtained in the following way: $I = (7.9 \pm 0.3) \times 10^{-4}$ M s⁻¹ was adopted from the kinetic runs. $2k_t$ was expressed in Arrhenius form, and the parameters $\log (A_t/M^{-1} s^{-1}) = 11.4 \pm 0.3$ and $E_t = (9.0 \pm 1.5)$ kJ/mol were extracted from $2k_t$ as given in Table II combined with termination constants and diffusion coefficient measured at -60, -40, and -30 °C. Further, an Arrhenius form of k_2 was assumed, and A_2 , E_2 , and a scaling constant were treated as free parameters of the fit. This lead to $\log (A_2/s^{-1}) = 14.0 \pm 0.5$ and $E_2 = (54.5 \pm 2.0)$ kJ/mol. Due to the uncertainties of the estimation procedure the actual errors may exceed the statistical errors given. Nevertheless, the Arrhenius parameters fit nicely into a series for other acyl radical decarbonylations.^{3,14,21} In particular, the activation energy for the decarbonylation of 2-methylpropanoyl is intermediate between that of propanoyl (61



Figure 4. Space-filling models of tert-butyl and isopropyl radicals.

kJ/mol) and 2,2-dimethylpropanoyl (39 kJ/mol) and demonstrates the influence of the degree of stabilization of the resulting alkyl radical.¹⁴ From the Arrhenius parameters, $k(300 \text{ K}) = 1.5 \times 10^4$ s⁻¹ is estimated. Compared with data for other decarbonylations¹⁴ the reaction of 2-methylpropanoyl is rather slow and extends the range of such "clock" reactions measured hitherto in liquid solutions toward the long-time region.¹⁴

Finally, we turn to a discussion of the ratios of disproportionation to combination of Table I. Since self-termination is diffusion controlled these ratios must reflect a partitioning of encountering radical pairs between two reaction channels. Previously, for the related cases of *tert*-butyl and isopropylol radicals a large dependence of P_d/P_c on solvent viscosity was found.^{1,3,12} It was explained in terms of anisotropic reorientational motions of the radicals in the encountering pairs combined with anisotropies of reactivities.^{1,3} For isopropyl radicals P_d/P_c varies only slightly with temperature and solvent viscosity. However, as will be evident, this is quite expected from the previous model and the particular structure of the radical. The model predicts that for small reactive surface fractions, high reactivities from reactive configurations, and negligible diffusive separation P_d/P_c can be written as^{1,3}

$$P_{\rm d}/P_{\rm c} = (C/2)(1 + b/a)$$
 (13)

where C is approximated by the ratio of disproportionation to combination in the gas phase and a and b are rate constants for reorientation of the radical's $2p_z$ orbital (a) and the methyl hydrogen bonds (b) in space. Space-filling models for *tert*-butyl and isopropyl radicals are shown in Figure 4. Both radicals can roughly be represented by rotational ellipsoids. For the oblate *tert*-butyl radical we can write

$$a = 2\tau_l^{-1} \qquad b = 2\tau_l^{-1} + \tau_k^{-1} \tag{14}$$

whereas for the prolate isopropyl

$$a = \tau_l^{-1} + \tau_k^{-1} \qquad b = \tau_l^{-1} + 2\tau_k^{-1} \tag{15}$$

where τ_l and τ_k are reorientational correlation times for motions about the axes l and k of Figure 4. Now, for *tert*-butyl and isopropylol radicals motion about axis k is only slightly hindered by the surrounding solvent molecules and is little affected by the viscosity whereas motion about axes l is strongly hindered. Insertion of (14) into (13) gives for this case

$$P_{\rm d}/P_{\rm c} = C \left(1 + \frac{\tau_1}{4\tau_{\rm k}} \right) \tag{16}$$

With $\tau_l = A\eta + B$ and τ_k nearly independent of viscosity and smaller than τ_l this leads to the observed behavior.¹⁻³ On the other hand, for isopropyl motion about the axis *l* is rather free, i.e., τ_l << τ_k . Then (15) and (13) yield $P_d/P_c \cong C$ and are viscosity independent, as is observed. Thus, the divergent disproportionation to combination behavior of *tert*-butyl and isopropylol vs. isopropyl radicals is well explained in terms of the reorientational model.

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Registry No. *i*-Pr₂C=O, 565-80-0; *i*-Pr-, 2025-55-0; (CH₃)₂CH-Ċ=O, 35586-36-8.