C_2H_5OH suggest that such barriers[24] are comparable in height in both species; thus, there exists little evidence to conclude that the elimination barrier is significantly different in the species $CH_3OH_2^+$ and $C_2H_5OH_2^+$. The enhanced product translation of CH_3CHOH^+ relative to $HCHOH^+$ and the lower H_2:HD ratio in the present case are consistent with a higher fraction of the $C_2H_5OH_2^+$ products decaying over the elimination barrier rather than tunneling through the barrier.

The qualitatively different angular distributions for decay of $C_2H_5OH_2^+$ by C–O bond cleavage and elimination of H_2 across the C–O bond are indicative of significantly different transition states for the two decay channels originating from the same precursor. The classic paper of Miller, Safron, and Herschbach[25] indicates that, when the orbital angular momentum of the approaching reagents creates a complex of high angular momentum $\mathcal{J}$ which then decays by disposing of $\mathcal{J}$ as relative product angular momentum, a prolate symmetric top decomposing along its symmetry axis yields a forward–backward peaked angular distribution, while an oblate top yields a sideways peaked distribution.

Because the decomposing ion $C_2H_5OH_2^+$ in the present work is created as one of the products of a bimolecular reaction, the dynamics of the proton-transfer reaction dictate the amount of rotational excitation which the products carry away. The elastic spectator (ES) model of Herschbach[26] predicts a high degree of angular momentum polarization in atom plus diatomic molecular reactions as a function of the skew angle β of the potential energy surface. In the present case, the "spectator" is a diatomic molecule which can carry away angular momentum, and thus the predictions of the ES model are not directly applicable. Consideration of the transition states for C–O bond cleavage and H_2 elimination indicate that, in the former case, the transition state should look quite prolate, with separation occurring along the C–C–O axis, while, in the latter case, the H_2 must separate along a coordinate essentially perpendicular to the axis defined by the nearly collinear arrangement of the three heavy atoms. Very strong peaking would be observed in the angular distributions if the three heavy atoms rotated in a plane containing the initial relative velocity vector. Although there are no clear angular momentum constraints to ensure such a correlation, the angular distributions of the products suggest that the initial proton-transfer reaction does polarize the rotational angular momentum of $C_2H_5OH_2^+$ sufficiently to lead to the characteristic symmetries that we observe. The molecular complexity of the system as well as the sequential nature of the processes leading to products make specific identification of such a mechanism quite speculative and we make no further attempt to rationalize our observations.

The dynamics of the proton-transfer reactions of HCO^+ with small aliphatic alcohols appear to be rather similar; the unimolecular decay channels also display similar behavior, with C–O bond cleavage proceeding through a "loose" transition state while the elimination reaction involves a significant barrier, through which quantum-mechanical tunneling appears facile. The precise magnitude of this barrier is uncertain and theoretical calculations to define the barrier more precisely would be of interest. Even more interesting, however, would be the development of appropriate pseudopotentials which could describe the dynamics of the proton-transfer reaction with a small number of degrees of freedom. The present work suggests that such a description would be useful and perhaps generally applicable.

Acknowledgment. We gratefully acknowledge support of this research by the U.S. Department of Energy. We wish to thank Mr. Robert Sandor for assistance with the data acquisition.

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Self-Termination and Electronic Spectra of Substituted Benzyl Radicals in Solution

Rodney F. C. Claridge* and Hanns Fischer

Physikalisch-Chemisches Institut der Universität Zürich, CH 8057 Zürich, Switzerland *(Received: December 26, 1982)*

Several substituted benzyl radicals have been generated in liquid cyclohexane by the photolysis of symmetrically substituted dibenzyl ketones. The rate constants for self-termination to substituted bibenzyls, and absorption spectra of the transient radicals, have been measured by optical modulation spectroscopy. The termination rates are generally well described by the von Smoluchowski equation with a spin factor of $^1/_4$. Deviations are discussed in terms of steric retardation and the unreliability of the estimated reaction diameters of radicals with bulky substituent groups. Absorption spectra of the three monomethyl-, the three monochloro-, two dichloro-, and the three monomethoxybenzyl radicals demonstrate the influence of the substituents on the energy levels of the benzyl system.

Recent kinetic investigations have shown that the reactions of transient hydrocarbon radicals in solution occur very rapidly at, or near, the magnitude expected for translational diffusion.[1-4] Accurate measurements in many solvents and over a wide range of viscosity and temperature of the bimolecular self-termination reactions

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* On leave from the Chemistry Department, University of Canterbury, Christchurch, New Zealand. Address correspondence to this author at this address.

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of the two carbon-centered radicals, *tert*-butyl and benzyl, confirm that the data are perfectly described by the von Smoluchowski equation

$$2k_r^{D} = (8 \times 10^3)\pi\sigma\rho DN \qquad (1)$$

when standard procedures for estimating the parameters are adopted.[5-8] The diffusion coefficient, D, of the radical is approximated by that of the corresponding hydrocarbon, RH; the reaction diameter, ρ, is estimated from molecular or molar volumes; the spin statistical factor, $\sigma = {}^1/_4$, is used since only singlet encounters will lead to ground-state products. The failure to observe termination to triplet-state benzil from benzoyl radical shows that triplet termination is kinetically unimportant.[9]

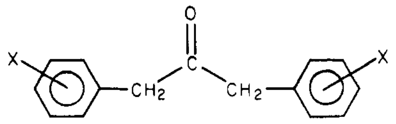
Similar procedures have been successfully applied to a number of systems by other authors indicating that these reactions are completely controlled by diffusion and spin statistics.[10,11]

Substituted benzyl radicals, for which steric hindrance may influence the rate of termination, have not been subjected to such detailed studies. Griller[12] has shown that the 2,4,6-tri-*tert*-butylbenzyl radical in di-*tert*-butyl peroxide solution is transient, with a rate constant for self-termination of $(5 \pm 2) \times 10^8$ L mol^{-1} s^{-1} at room temperature. Although this rate is probably close to the diffusion-controlled limit in this solvent, no comparison has been made with a rate calculated from the diffusion equation. The α,α-di-*tert*-butylbenzyl[13] and perchlorobenzyl radicals,[14] which for steric reasons adopt a "perpendicular" structure, where the benzene ring is no longer in conjugation with the unpaired electron, are persistent, the latter radical having a lifetime in solution of months. For these radicals, diffusion is apparently not the rate-controlling factor.

In this paper we now extend the test of the validity of eq 1 to the termination reactions of a series of ring-substituted benzyl radicals in cyclohexane solution. Benzyl radicals with methyl, chlorine, or methoxy groups substituted into the ring 3- or 4-positions serve as control compounds for the 2-substituted analogues where small effects may be expected to be observed. The parameters for estimation of the theoretical diffusion-controlled rate are also determined. Diffusion coefficients of the related hydrocarbons have been measured under closely controlled conditions. Reaction diameters must as yet be calculated by a number of empirical methods and are the most unreliable part of the determination of the theoretical rate. Since all compounds are treated in the same way, the relative rates should be reliable and deviations of the observed rates attributed to steric or other factors influencing the termination.

In these kinetic investigations harmonic modulation spectroscopy[8] has been used, utilizing the photolysis of the substituted dibenzyl ketones as the source of radicals. The technique has also allowed the recording of hitherto unavailable optical absorption spectra of transient species in solution. The principles of the technique based on the work of Hunziker[15] on the study of radicals in the gas phase and the extensions by Günthard[16] and Paul[11] to the liquid-phase electron spin resonance investigations are described in detail in ref 8.

TABLE I: nπ* Transition Maxima and Intensities for Substituted Dibenzyl Ketones in Cyclohexane



1,3-bis(X-phenyl)propan-2-one

X	λ_{max}, nm	ϵ_K
H (dibenzyl ketone)	294	245
4-methyl	295	310
3-methyl	292	250
2-methyl	296	241
4-chloro	295	247
3-chloro	296	237
2-chloro	295 (sh)	159
2,4-dichloro	295 (sh)	241
2,6-dichloro	295 (sh)	103
4-methoxy	300 (sh)	572
3-methoxy	300 (sh)	456
2-methoxy	300 (sh)	289

Electronic spectra of some substituted benzyl radicals produced under a variety of conditions have been described by several authors.[17-25] The spectra resemble those of benzyl with small shifts of the maxima to longer wavelengths. Fluorescence and excitation spectra of methyl-substituted benzyl radicals in solid matrices have been used to determine the symmetry character and energy of the ground and excited states,[19] and under conditions where good resolution has been obtained a vibrational analysis of the first band has been carried out.[20]

While the two methods of radical production used in the solid state, photolysis of the hydrocarbon and dissociative electron attachment from the benzyl chloride, yield nearly identical spectra in the visible and near-ultraviolet region, a discrepancy in the absorption of the far-ultraviolet band is apparent.[22,23] A similar dependence of the far-ultraviolet band of transient benzyl radicals on the concentration of benzyl chloride was observed in pulsed electron experiments in solution.[26] An explanation in terms of complexing of the benzyl radical with the solute seems improbable and shows the need for a method of radical production which yields spectra free of interference from the solute. The modulation spectroscopic technique has

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been shown to satisfy this criterion.

We report the transient absorption spectra of the monomethylbenzyl, monochlorobenzyl, monomethoxybenzyl, and two dichlorobenzyl radicals generated by modulated photolysis in liquid cyclohexane. Where the results overlap with previous investigations using other techniques of radical generation they confirm the validity of photolysis of the ketone as a method of producing authentic spectra free from absorption of the parent or other products.

Experimental Section

Substituted dibenzyl ketones (1,3-bis(substituted phenyl)propan-2-one) were prepared by a modified Claisen condensation.[27] Lead salts of the corresponding substituted phenylacetic acid were heated under vacuum (<1 mm Hg) and the ketones distilled. Recrystallization from ethanol or ethanol–water mixture resulted in pure white crystalline solids. The two low-melting ketones (1,3-bis(3-methylphenyl)propan-2-one and 1,3-bis(3-methoxyphenyl)propan-2-one were purified by sublimation under vacuum. Purity was assessed by comparison of the melting points with literature values where available, NMR, and UV adsorption. Dibenzyl ketone from Fluka A.G. (Buchs) was recrystallized from hexane before use. Spectroscopic-grade cyclohexane (E. Merck A.G. Darmstadt) was used for all spectroscopic and kinetic measurements. Table I lists the ketones prepared with the absorption maxima and extinction coefficient of the characteristic $n\pi^*$ transition.

The apparatus for modulation transient spectroscopy described in detail by Huggenberger[8,9] was used. Solutions of the ketone, flowed through a thermostatically controlled cell (0.5 × 0.5 mm cross section), were photolyzed with light from a 1000-W Hg–/Xe arc lamp. The light, focused onto the cell by a Suprasil lens and filtered by a cobalt/nickel sulfate solution to restrict adsorption to the $n\pi^*$ band of the ketone, was modulated sinusoidally by a variable-frequency disk chopper immediately in front of the lens. Light from a dc-powered 450-W Xe arc served as the analyzing beam and was focused through the photolysis cell, perpendicular to the photolysis beam, onto the slits of a grating monochromator. The output of the photomultiplier was taken either directly to the input of a phase-sensitive detector or through an analog voltage divider whose output was proportional to the ratio of the ac to dc components of the photomultiplier output. The reference signal was provided from the chopper. A solution of the appropriate ketone, with concentration in the range (1–3) × 10^{-3} mol L^{-1}, such that <10% of the photolysis light was absorbed in the cell, was deaerated prior to use by purging with Ar gas. The flow rate, typically 1 mL min^{-1}, was chosen to give the optimum signal to noise.

Diffusion coefficients of hydrocarbons in cyclohexane were determined by a comparatively rapid and accurate method based on the axial dispersion of a solute in laminar flow through a capillary. The apparatus, utilizing components of conventional high-pressure liquid chromatography, has been described in detail.[9]

Results and Discussion

The experimental data from the modulation experiment are a phase angle, φ_{exptl}, and a modulated absorbance (optical density), ΔD. The phase angle is the sum of the true phase delay, φ_{r}, between the photolysis light and the modulated absorption and an arbitrary phase angle, φ_0, which takes into account any constant phase shift within the instrumentation, such as a residual phase shift between the reference signal and the photolysis light. The amplitude of the modulation absorption is given by

$$\Delta D = \epsilon_{\mathrm{r}} l \Delta[\mathrm{R}] \qquad (2)$$

where $\Delta[\mathrm{R}]$ is the modulated amplitude of concentration, and ϵ_{r} is the decadic extinction coefficient at the chosen absorption maxima. In the results recorded herein analysis was carried out by using the strong absorption bands of the benzyl radicals in the near-ultraviolet between 315 and 325 nm.

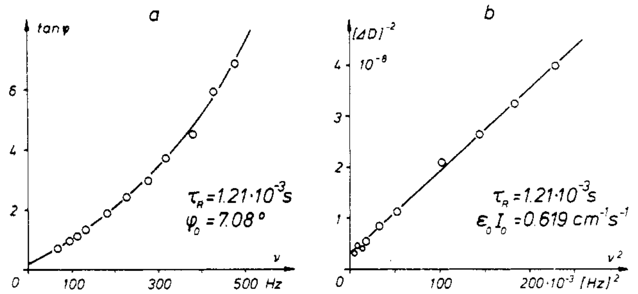

Figure 1. Frequency dependence of benzyl radicals in cyclohexane: (a) phase, (b) amplitude.

The solution of the differential equations for the reaction scheme of the photolysis of the benzyl ketone and termination to bibenzyl leads to the expressions

$$\tan\,(\varphi_{\mathrm{exptl}} - \varphi_0) = -\omega\tau_{\mathrm{r}} \qquad (3)$$

$$\Delta[\mathrm{R}] = \tfrac{1}{2}(\omega^2 + \tau_{\mathrm{r}}^{-2})^{1/2} \qquad (4)$$

A radical lifetime, τ_{r}, is defined in terms of k_{r}, the rate of self-termination, and I_0, the rate of radical formation.

$$\tau_{\mathrm{r}} = (4k_{\mathrm{r}}I_0)^{-1/2} \qquad (5)$$

Making use of eq 2, one may write

$$(\Delta D)^{-2} = 4(\epsilon_{\mathrm{r}} l I_0)^{-2}\omega^2 + 4(\epsilon_{\mathrm{r}} l I_0 \tau_{\mathrm{r}})^{-2} \qquad (6)$$

The radical lifetime, τ_{r}, and the arbitrary phase angle, φ_0, are extracted from eq 3 by least-squares fitting. Equation 6 is independent of the arbitrary phase angle and yields the lifetime, τ_{r}, and the product, $\epsilon_{\mathrm{r}} I_0$, from linear plots of ΔD^{-2} against ω^2. To obtain the extinction coefficient, ϵ_{r}, and the termination rate, k_{r}, the rate of radical formation, I_0, is determined from a separate experiment.[8]

Kinetics of Self-Termination. Utilizing the methods outlined above, we determined the rate constants for self-termination of benzyl and the substituted benzyl radicals in cyclohexane solution at 26 °C. Figure 1 shows the results of an experiment with 1.76 × 10^{-3} mol L^{-1} dibenzyl ketone in cyclohexane and illustrates the degree of fit of the data to the theoretical expression. The fourth column of Table II presents the data for the experimental rates.

The rate of self-termination for benzyl, 4.6 × 10^9 L mol^{-1} s^{-1}, is at the upper limit of the range of recent measurements under similar conditions of solvent and temperature. Huggenberger,[8] using the same modulated optical spectroscopic technique, obtained $2k_{\mathrm{r}} = 3.6 \times 10^9$ L mol^{-1} s^{-1}. Hagemann and Schwarz[28] obtained $2k_{\mathrm{r}} = 4 \times 10^9$ L mol^{-1} s^{-1} based on an assumed extinction coefficient = 12000 at 317 nm. Using a chemical technique, Burkhart[29] obtained $2k_{\mathrm{r}} = 4.0 \times 10^9$ L mol^{-1} s^{-1} while Lehni,[7] using ESR, obtained $2k_{\mathrm{r}} = 4.1 \times 10^9$ L mol^{-1} s^{-1}.

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TABLE II: Termination Rates of Substituted Benzyl Radicals in Cyclohexane at 295 K

radical	$\lambda_{\max}$, nm	ϵ_R, M^{-1} cm^{-1}	$10^{-9}2k_R$, m^{-1} s^{-1}	10^5D,[a] cm^2 s^{-1}	10^{-9} × $2k_R{}^D$,[b] M^{-1} s^{-1}	$2k_R/2k_R{}^D$	I_0[c]	ϕ[d]
benzyl	316	8800 ± 600	4.6 ± 0.3	1.68 ± 0.05	3.74	1.23	1	1
4-methylbenzyl	320	7400 ± 200	3.7 ± 0.1	1.51 ± 0.03	3.56	1.04	1.32	1.04
3-methylbenzyl	321	6800 ± 800	4.0 ± 0.8	1.39 ± 0.05	3.27	1.22	0.96	0.94
2-methylbenzyl	321.5	10200 ± 200	4.4 ± 0.1	1.36 ± 0.03	3.20	1.38	0.31	0.31
4-chlorobenzyl	317	7200 ± 150	3.7 ± 0.3	1.44 ± 0.04	3.36	1.10	0.69	0.69
3-chlorobenzyl	324	7100 ± 100	3.8 ± 0.6	1.40 ± 0.02	3.27	1.16	0.43	0.45
2-chlorobenzyl	325	8100 ± 200	2.1 ± 0.2	1.40 ± 0.02	3.26	0.64	0.21	0.32
2,6-dichlorobenzyl	336.5	5000 ± 200	2.9 ± 0.4	1.23 ± 0.03	2.97	0.98	0.10	0.23
2,4-dichlorobenzyl	330	5000 ± 100	2.4 ± 0.3	1.24 ± 0.01	3.00	0.80	0.08	0.09
4-methoxybenzyl	321	2900 ± 300	3.2 ± 0.3	1.37 ± 0.06	3.33	0.97	2.10	0.89
3-methoxybenzyl	321	1900 ± 400	3.4 ± 0.8	1.35 ± 0.04	3.25	1.06	0.86	0.46
2-methoxybenzyl	332	3600 ± 300	2.2 ± 0.6	1.30 ± 0.04	3.15	0.71	0.42	0.35

[a] Experimental values of diffusion coefficient of corresponding substituted toluene. [b] Calculated by using the von Smolouchowski equation. [c] Relative rate of radical generation; I_0(benzyl) = 1. [d] Relative quantum yield: ϕ(benzyl) = 1.

The agreement between the benzyl rate determined in this experiment and the previous results gives confidence that the data for the other substituted benzyl radicals, which are previously unreported, are reliable.

It is recognized that the self-termination of small radicals, including benzyl, in solution are almost, if not completely, diffusion controlled. The question now arises whether the slower rates of some of the substituted benzyl radicals, especially 2-chloro- and 2-methoxybenzyl, are deviations from complete diffusion control caused by steric factors.

In order to assess the experimental termination rates, comparison is made with the theoretical diffusion-controlled rates. To calculate the limiting rates, via the von Smoluchowski equation, eq 1, estimates of the diffusion coefficients, D, the mean reaction diameter of the radical, ρ, and the spin statistical factor, σ, are required. Radical diffusion coefficients are usually best approximated by the diffusion coefficients of the corresponding hydrocarbon. The fifth column of Table II lists the diffusion coefficients of the corresponding substituted toluene measured in cyclohexane at 26 °C. The data are the average of at least four determinations and are reliable to 0.1%. The experimental value for toluene in cyclohexane at 26 °C is in good accord with the values extracted from the literature[30,31] and confirms the reliability of this method of measurements of diffusion coefficients.

The estimate of the reaction distance of the radical is more difficult. Following the procedure used by Lehn,[7] we have estimated ρ in three ways: (a) from the molar volume of the corresponding toluene and the space filling factor for cubic close packing,[32] (b) by a simple volume increment method,[33] and(c) by a volume increment method using LeBas increments.[34] As an example, the molar volume method gives ρ = 0.650, 0.652, and 0.652 nm for the 2-, 3-, and 4-chlorobenzyl radicals, respectively, while the empirical volume increment methods yield 0.598 and 0.608 nm independent of the position of substitution. In the absence of any better method, an average of the three values was taken. These average values range from ρ = 0.590 nm for benzyl to ρ = 0.640 nm for 2,6-dichlorobenzyl.

A spin statistical factor $\sigma = {}^1/_4$ was used, it being assumed that reaction only to singlet ground-state products was possible. The sixth and seventh columns of Table II list the values of the calculated rate constants, $2k_r{}^D$, and the ratio $2k_r/(2k_r{}^D)$. The calculated values do not show as wide a variation as the experimentally determined rate constants presumably because in the calculation the assumed reaction distance makes no allowance for the position of the substituent. If there were to be any steric restriction to termination caused by the bulky groups, making the rate slightly less than diffusion controlled, it would be expected that the effect would be greatest for the 2-substituted benzyls. The data indicate that indeed the 2-chlorobenzyl and the 2-methoxybenzyl appear to be less than diffusion controlled.

A recent time-resolved electron spin resonance determination of the self-termination of the 2-chlorobenzyl radical yielded $2k_r$ = (2.43 ± 0.85) × 10^9 L mol^{-1} s^{-1} in cyclohexane containing 4% (v/v) of benzol at 25 °C, confirming the low value obtained in this work.[35]

That the termination of 2-methylbenzyl is at least as rapid as predicted by the von Smoluchowski equation might be accounted for by invoking the possibility of intramolecular hydrogen transfer from the CH_3 group to the CH_2 group, facilitating termination through either group. However, if steric factors were important, the termination rates at 2,4-dichloro- and 2,6-dichlorobenzyl radicals should be much less than the diffusion-controlled limit. That this is not the case weighs against the steric arguments. It should however be pointed out that these are the least reliable measurements because of the low radical concentration by photolysis (see later section).

It seems best to assume that the termination reactions are almost completely diffusion controlled and that the deviation of the ratio $2k_r/(2k_r{}^D)$ arises from overestimates of the thermination rate from the von Smoluchowski equation. The most serious discrepancy is in the estimation of the reaction diameter. The first of the methods used, calculation based on the molar volume, is the only one which makes any allowance for bulky substituents. The other two methods rely entirely on additive factors for the atoms irrespective of their arrangement. Until more reliable estimates of the reaction diameter can be made no firm conclusion can be drawn; conversely, reliable rate data could be used to establish better estimates of the reaction parameters and to test the reliability of the von Smoluchowski equation (based on diffusing spheres) to describe the diffusion of bulky radicals.

Spectra. Spectra of the transient radical were recorded at low modulation frequencies (90–95 Hz) with the ketone concentration in the range (1–3) × 10^{-3} mol L^{-1} in cyclo-

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TABLE III: Observed 0_0^0 Transitions of Substituted Benzyl Radicals

radical	$4^2B_2 \leftarrow X^2B_2$, nm (eV)	$2^2A_2 \leftarrow X^2B_2$, nm (eV)	$1^2A_2 \leftarrow X^2A_2$, nm (eV)
benzyl	258 (4.81)	316 (3.92)	463 (2.68)
4-methylbenzyl	257 (4.64)	320 (3.87)	467 (2.66)
3-methylbenzyl	263 (4.71)	321 (3.86)	472 (2.63)
2-methylbenzyl	261.5 (4.74)	321.5 (3.86)	475 (2.61)
4-chlorobenzyl	269 (4.61)	317 (3.91)	473 (2.62)
3-chlorobenzyl	261 (4.75)	324 (3.83)	478 (2.59)
2-chlorobenzyl	259 (4.79)	325 (3.82)	481 (2.58)
2,4-dichlorobenzyl	268 (4.63)	330 (3.76)	~510 (2.43)
2,6-dichlorobenzyl	258 (4.81)	324 (3.83)	~520 (2.38)
4-methoxybenzyl	263 (4.71)	321 (3.86)	485 (2.56)
3-methoxybenzyl	258 (4.81)	323 (3.84)	511 (2.43)
2-methoxybenzyl	268 (4.63)	332 (3.73)	484 (2.56)

hexane at 26 °C by using the voltage analog divider. Solution flow rates were of the order of 1 mL min^{-1}. The amplitude signal was recorded directly with monochromator scan rates of about 20 nm min^{-1}, a time constant of typically 1 s, and resolution of the monochromator set at 1 nm. The photolysis of dibenzyl ketone gave a spectrum identical with that reported by Huggenberger[8] in good agreement with previously reported specta recorded under a variety of conditions. The principal features of the spectrum are a strong transition at 258 nm, a band system with three maxima the most intense at 316 nm, and a very weak structured band in the visible extending out to a last weak maxima at 462 nm. These band systems have been identified with 0_0^0 transitions from the $^2B_2$ ground electronic state to the 4^2B_2, 2^2A_2, and 1^2A_2 excited states, respectively.[36]

The two most prominent absorption maxima of the long-wavelength, $1^2A_2 \leftarrow X^2B_2$, transition are assigned on the basis of the work of Leach,[37,38] who has shown that the non-mirror-image symmetry of the fluorescence and the excitation spectra of benzyl type radicals is caused by vibronic mixing of the asymmetric vibrational mode, 6b, and the in-plane deformation, 18b, of the 1^2A_2 state with the ground vibrational level of the 2^2B_2 state which was shown to lie 460 cm^{-1} above the first excited state. The observed band at 453 nm in our spectrum is an overlap of the band labeled A^2 by Leach, arising from the vibronic interaction, and the unmixed $6a_0^1$ transition. The band at 437 nm is assigned to the transition to the first level of the totally symmetric vibrational mode, $12a_0^1$.

The absorption spectra of the three monomethylbenzyl radicals obtained by photolyzing the appropriate ketone under conditions similar to those above, are in excellent agreement with the solid-state fluorescence spectra previously recorded.[19,22,23] The similarity of these spectra to those of benzyl, particularly in the ultraviolet region, show that the C_{2v} symmetry is not greatly affected by methyl substitution. The positions of the maxima of the 0_0^0 bands of the transitions, shown in Table III, are all shifted to the red with respect to those of the benzyl radical.

In contrast to the fluorescence excitation spectrum at 77 K[23] for the 4-methylbenzyl radical we find no evidence of a transition to the 3^2B_2 state near 290 nm. The long-wavelength band shows considerable similarity to the benzyl radical spectrum in this region as expected on symmetry grounds. The 0_0^0 band is weak; the next two stronger bands can be assigned by analogy with the benzyl spectrum; the 457-nm band can be assigned to the admixture of an A^2 type band and the $6a_0^1$ band, and the 442-nm band to the $12a_0^1$ transition. These assignments which place the 6a′ and 12a′ levels 470 and 1210 cm^{-1} above the ground vibrational level of the upper state are compatible with the known vibrational assignment of *p*-xylene.[39-41]

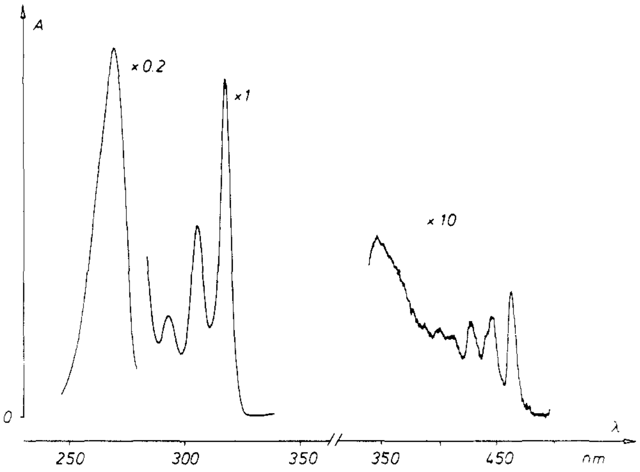

Figure 2. Absorption spectrum of 4-chlorobenzyl in cyclohexane.

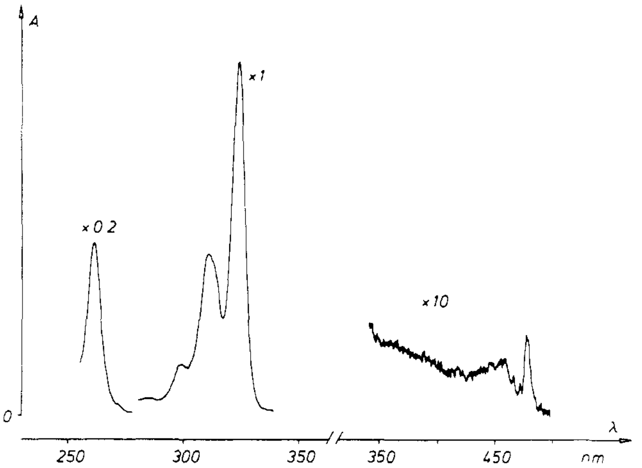

Figure 3. Absorption spectrum of 3-chlorobenzyl in cyclohexane.

While the ultraviolet bands of 3-methylbenzyl and 2-methylbenzyl are similar to benzyl and 4-methylbenzyl, the long-wavelength bands are not, presumably because of the lower vibrational symmetry. The 0_0^0 band is now the strongest with little resolution elsewhere. The broad maximum 350–400 nm in the 3-methylbenzyl spectrum resembles the weak absorption spectrum of the *m*-benzyl biradical, described by Migirdicyan,[42] produced in low yield

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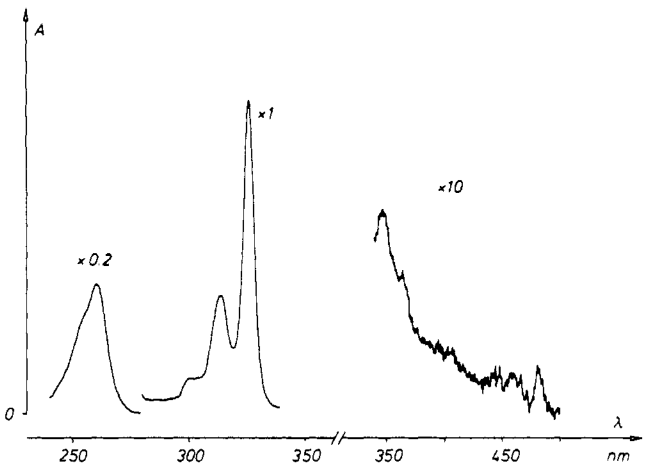

Figure 4. Absorption spectrum of 4-chlorobenzyl in cyclohexane.

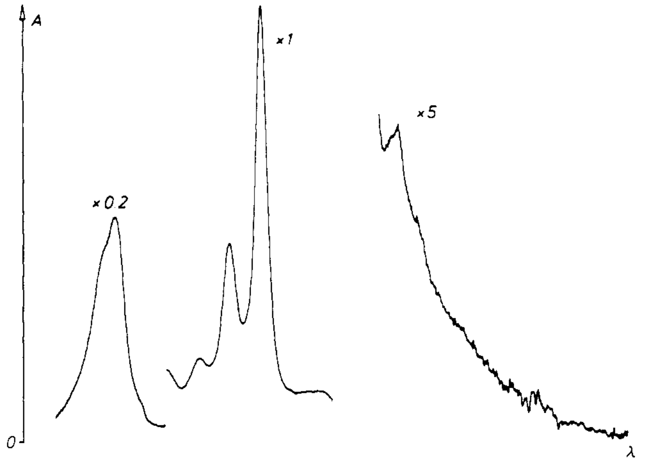

Figure 5. Absorption spectrum of 2,4-dichlorobenzyl in cyclohexane.

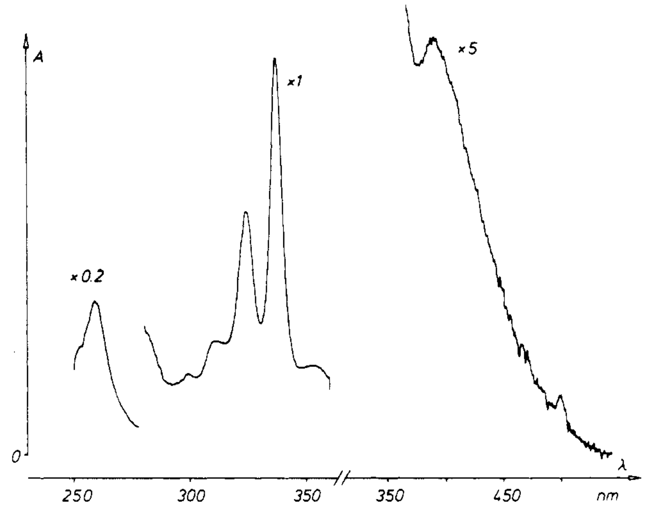

Figure 6. Aborption spectrum of 2,6-dichlorobenzyl in cyclohexane.

as a byproduct in photolysis in glassy matrices. It is, however, unlikely that a secondary product would contribute to absorption under the conditions of the present experiments.

Figures 2–6 show the spectra of the three monochlorobenzyl radicals and the two dichlorobenzyl radicals. To our knowledge these radicals have not been previously

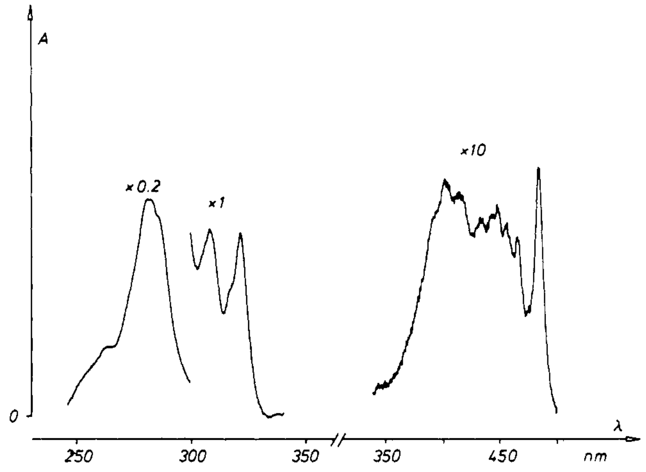

Figure 7. Absorption spectrum of 4-methoxybenzyl in cyclohexane.

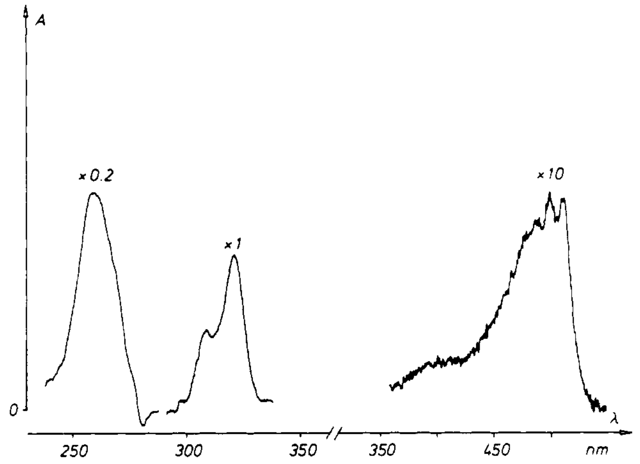

Figure 8. Absorption spectrum of 3-methoxybenzyl in cyclohexane.

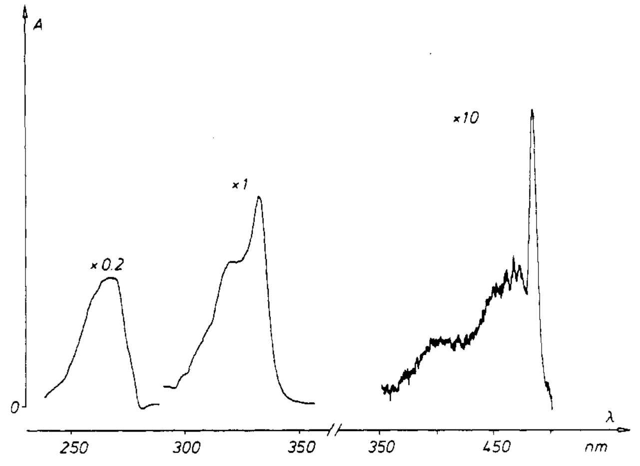

Figure 9. Absorption spectrum of 2-methoxybenzyl in cyclohexane.

reported. The spectra are all recognizably of the benzyl radical type showing that chlorine substitution does not greatly affect the electronic energy levels.

The 4-chlorobenzyl radical, like the 4-methylbenzyl radical, shows a large red shift of the far-UV maximum, but the near-UV band is not as greatly shifted. The 0_0^0 band of the visible transition is assigned as a shoulder at 473 nm on the side of the intense band at 463 nm. By analogy with benzyl and 4-methylbenzyl we tentatively assign the 463-nm band to the A^2 type and the $6a_0^1$ transitions, and the 446-nm band to the $12a_0^1$ transition.

Two chlorines attached to the aromatic ring cause all the maxima to be shifted to longer wavelengths; the visible

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bands now no longer show any resolved structure so that the 0_0^0 bands can only be approximated by the end of the spectrum.

Figures 7–9 show the spectra of the three monomethoxybenzyl radicals. The addition of a methoxy group into the aromatic ring does alter the spectrum, although the basic features of the benzyl radical type spectrum remain with three distinguishable band systems. For lack of any other evidence we assume that the order of the electronic energy levels remains unchanged from that of benzyl and that the same assignments can be made.

All of the spectra recorded appear to be free of interference from absorption by any intermediate product such as the semibenzenes[43] (methylenecyclohexadienes), or the ultimate product, bibenzyl, in the region above 290 nm. The wavelengths and the extinction coefficients for the $2^2A_2 \leftarrow X^2B_2$ transition are shown in the second and third columns of Table II. For benzyl, the values obtained are identical with those of Huggenberger[1] and are in good agreement with the previous literature values. Monomethyl and chloro substitution make small changes to the extinction coefficient from that of benzyl. In both series the 2-substituted radical has the largest value, in accord with the oscillator strengths calculated by using a restricted Hartree–Fock open-shell procedure in a CNDO/S system.[23,44]

The addition of a second chlorine lowers the extinction to about 5000. Methoxy substituents cause an even greater reduction; again in this series the 2-methoxybenzyl radical has the largest of the three values and 3-methoxybenzyl the lowest.

The relative intensities of the three observable band systems can be obtained from the spectra and show that in all cases the far-UV, $4^2B_2 \leftarrow X^2B_2$, transition is the most intense band. Where comparable data are available, as for the methylbenzyls, our data agree substantially with the solid-state excitation fluorescence spectra of the methylbenzyl radicals prepared by photolysis of the hydrocarbon.[19,23] Where the radicals have been prepared by dissociative electron attachment to a benzyl chloride the excitation spectra show a much smaller absorption in this region.[22] A dependence of the absorption at 258 nm on the concentration of benzyl chloride observed in the spectra of transient benzyl radicals produced in solution pulsed radiolysis experiments led Sangster[26] to propose the formation of complexes between the benzyl chloride and the benzyl radical altering the relative transition probability between the band systems.

We have been able to reproduce these results when benzyl chloride or benzyl alcohol was added to the ketone solution. However, a similar reduction of the apparent absorption of the 258-nm band was observed when benzyl chloride, or any material with absorption in the region less than 280 nm, was placed in the analyzing beam, either before or after the photolysis cell. When the absorbance of this filter solution was >1.8, a reduction of the absorption of the 258-nm band was observed. Hence, we believe that the discrepancies of the relative intensities of the far-UV bands between the various published spectra are due to self-adsorption effects and probably nonlinear response of the photomultiplier rather than complex formation.

Quantum Yield. On the assumption that the mechanism of radical formation is the same for each ketone, that is, absorption through the $n\pi^*$ transition of the carbonyl group and subsequent decomposition of the excited state, the relative quantum yields for radical formation can be calculated by comparison of the rate of radical formation, I_0, under conditions of identical concentration and constant light flux. In all these experiments the conditions are such that Beer's law applies. Assuming that the absorption bands of each ketone (λ_{max} in the range 294–300 nm) are all equally irradiated, the relative quantum yield is then approximately the relative rate of formation of radicals divided by the extinction coefficient of the $n\pi^*$ transition of the appropriate ketone (Table I). Table II shows these results.

The values obtained show wide variations, ranging from 1.04 for 4-methylbenzyl to 0.085 for 2,4-dichlorobenzyl, relative to benzyl (ϕ = 1.00). Some confidence in the reliability of these values comes from the work of Robbins and Eastman,[45] who determined from product analysis the absolute quantum yields for benzyl (0.70), 4-methylbenzyl (0.71), and 4-methoxybenzyl (0.65). These values are in the ratio 1.00:1.01:0.93, in good agreement with the values reported in this work.

For each of the three series of monosubstituted benzyl radicals the quantum yields decrease in the order 4-X-benzyl > 3-X-benzyl > 2-X-benzyl. Electron spin resonance evidence[35] indicates that there are no long-lived acyl radicals formed under the conditions of these experiments, which suggests that the quantum yield reflects changes in the excitation–deexcitation process rather than in the subsequent decomposition and termination steps. The very low quantum yields for the formation of the dichlorobenzyl radicals support the view that increasing complexity allows the possibility of mixing of orbitals from the substituents providing additional paths for deexcitation.

Conclusion

The use of modulated optical spectroscopy has allowed the measurement of the termination kinetics and the recording of the optical absorption spectra of the transient substituted benzyl radicals. In all cases the rate of termination is close to that predicted for diffusion by the von Smoluchowski equation. The slight deviation of the 2-chloro- and 2-methoxybenzyl radicals from diffusion control is more apparent than real and reflects the inaccuracy in estimation of the reaction parameters, ρ, in the calculations. The observation of significant deviations through steric effects will await measurements on more highly substituted benzyl radicals.

The absorption spectra of the chlorobenzyl radicals indicate that chlorine substitution, like methyl substitution, makes only a minor perturbation to the electronic levels of the benzyl radical system and the band systems are readily correlated. Methoxy substitution makes greater changes although the main band systems are still identifiable. Calculations of these effects of substitution on the benzyl radical are in progress.

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Registry No. Dibenzyl ketone, 102-04-5; 1,3-bis(4-methylphenyl)propan-3-one, 70769-70-9; 1,3-bis(3-methylphenyl)propan-3-one, 83598-09-8; 1,3-bis(2-methylphenyl)propan-3-one, 23592-92-9; 1,3-bis(4-chlorophenyl)propan-3-one, 65622-34-6; 1,3-bis(3-chlorophenyl)propan-3-one, 59757-95-8; 1,3-bis(2-

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chlorophenyl)propan-3-one, 85150-76-1; 1,3-bis(2,4-dichlorophenyl)propan-3-one, 85150-77-2; 1,3-bis(2,6-dichlorophenyl)propan-3-one, 85150-78-3; 1,3-bis(4-methoxyphenyl)propan-3-one, 29903-09-1; 1,3-bis(3-methoxyphenyl)propan-3-one, 56438-64-3; 1,3-bis(2-methoxyphenyl)propan-3-one, 85150-79-4; benzyl radical, 2154-56-5; 4-methylbenzyl radical, 2348-52-9; 3-methylbenzyl radical, 2348-47-2; 2-methylbenzyl radical, 2348-48-3; 4-chlorobenzyl radical, 3327-51-3; 3-chlorobenzyl radical, 3327-52-4; 2-chlorobenzyl radical, 3327-53-5; 2,6-dichlorobenzyl radical, 85150-80-7; 2,4-dichlorobenzyl radical, 85150-81-8; 4-methoxybenzyl radical, 3494-45-9; 3-methoxybenzyl radical, 51053-85-1; 2-methoxybenzyl radical, 85150-82-9.

Ion-Exchange Kinetics in Zeolite A

D. Drummond, A. De Jonge,[†] and L. V. C. Rees*

Physical Chemistry Laboratories, Imperial College of Science and Technology, London, England SW7 2AY

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The kinetics of Na → Ca exchange in zeolite A has been measured at 25 °C. The rates of complete replacement of Na^+ by Ca^{2+} have been obtained and, also, the rates of small incremental replacements over the range of zeolite composition from pure sodium to 90% calcium have been measured. The kinetics of the reverse exchange has also been studied to a limited extent. All of these kinetics have been analyzed by using the Paterson solutions of the diffusion equation. In a separate study the degree of hydrolysis of zeolite A as a function of pH has been ascertained.

Introduction

Zeolite A, in its sodium form, has recently been introduced in extensive quantities as a builder in detergents. In a recent paper[1] the high selectivities of Na–A for Ca^{2+} and Mg^{2+} have been demonstrated. In this equilibrium study the thermodynamic quantities for these binary exchanges were obtained and polynomial expressions derived from which the binary isotherms at 25 and 65 °C could be calculated for any normality of solution phase. The more difficult ternary exchange was also studied for solutions which initially contained Ca^{2+}:Mg^{2+} ratios of 2:1, 1:1, and 1:2. An attempt was made to predict the ternary isotherms from the binary isotherms.

Although a high selectivity for both of these divalent ions is an essential feature in the use of zeolite A as a builder in detergents, it is also necessary for the removal of the divalent ions to be extremely rapid to prevent interactions with the surfactants present. Rapid removal of Ca^{2+} ions is readily accomplished if the Na–A cubes have side lengths of ~1 μm. The Ca^{2+} ion concentration is reduced to acceptable levels in ~20 s. The removal of Mg^{2+} ions is not so rapid but the higher concentration of Mg^{2+} which still exists after ~1 min is not a serious problem.

In this paper the kinetics of $Na^+ \rightleftharpoons Ca^{2+}$ exchange in zeolite A will be presented and the effect of the presence of Mg^{2+} ions on the exchange will be demonstrated. Also, zeolite A has one other important characteristic which enhances its suitability as a builder. It is readily hydrolyzed and so causes no environmental waste problems. The hydrolysis of zeolite A at various pH values will also be reported.

Experimental Section

In order to follow exchange times much greater than those which apply under detergency conditions, larger crystals of zeolite A were required. These large crystals were synthesized by using the Charnell method.[2] The crystals obtained were well-formed cubes of side lengths in the range 15–18 μm.

The kinetics of exchange were usually followed by means of sodium or calcium ion selective electrodes but some exchange rates were also measured, or compared, radiochemically with ^{22}Na as the radiotracer in the zeolite phase.

The uncertainty in F values decreases from 6.8% to 5.9% as F increases and leads to a corresponding uncertainty in log $\tilde{D}$ of 0.06–0.16. The uncertainty in the log $\tilde{D}$ vs. F plots should therefore be represented by an area. However, as the uncertainty in log $\tilde{D}$ is more significant, only error bars have been used as shown in Figure 4.

Results

In the first series of experiments $Na^+ \rightarrow Ca^{2+}$ exchange rates were measured at three different solution normalities. In these experiments the ratio of equivalents of cation (in this case Ca^{2+}) in the solution phase, M_s, to equivalents of cation (in this case Na^+) in the zeolite phase, M_z, was also varied from 100:1 down to 1:0.8. The three rate curves obtained are shown in Figure 1. These rate curves are very similar, indicating that differences in the parameters which were varied had little effect on the rate of exchange.

The rate curves in Figure 1 were analyzed by using the Paterson[3] solutions for limited volume diffusion in a manner similar to that described by Danes and Wolf.[4] It should be noted that the Paterson solution is derived for a constant diffusion coefficient. The Danes and Wolf treatment assumes an average constant D over the range of F from zero to each given value. In these solutions the parameter W is required where W is defined as

$$W = \frac{M_z}{M_s}\frac{d[Ca]_z}{d[Ca]_s} \tag{1}$$

$[Ca]_z$ and $[Ca]_s$ are the equivalent cation fractions of Ca^{2+} in the zeolite and solution phases, respectively. The re-

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[†] Present address: Department of Analytical Chemistry, Veszprem, Schönherz Z. u 12, Hungary.

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