Behavior of Thermally Generated Ketyl Radicals. Equilibrium Measurements[1]

Steven A. Weiner

Contribution from the Ford Motor Company, Scientific Research Staff, Dearborn, Michigan 48121. Received March 30, 1971

Abstract: The thermolysis of benzpinacols in solution at moderate temperatures (80–141°) yields benzophenone ketyl radicals. A bromine atom in the para position shifts the equilibrium to the radical relative to hydrogen while a methoxy group shifts the equilibrium to the pinacol. The benzpinacol yielding the more stable radical cleaves faster while the rate constant for radical termination is lower. The more stable the radical the higher the ratio of radical recombination to disproportionation. The activation energies for radical termination are approximately 3.5 kcal/mol higher in isopropyl alcohol than in benzene. Within experimental error (±30%), the fraction of cage reaction is independent of temperature.

In earlier work it had been shown that the termination constants for aromatic ketyl radicals, k_t, fit a Hammett σ–ρ plot in both benzene and isopropyl alcohol solutions.[2] For all ketyl radicals studied, the

$$(\mathrm{Ar})(\mathrm{Ar'})\mathrm{C(OH)C(OH)}(\mathrm{Ar})(\mathrm{Ar'}) \underset{k_t}{\overset{k_s}{\rightleftarrows}} 2(\mathrm{Ar})(\mathrm{Ar'})\dot{\mathrm{C}}(\mathrm{OH}) \quad (1)$$

Ia, $\mathrm{Ar} = \mathrm{Ar'} = C_6H_5$ IIa, $\mathrm{Ar} = \mathrm{Ar'} = C_6H_5$

termination constant in isopropyl alcohol was lower than in benzene. In both solvents the termination constants ranged over two orders of magnitude with none lower than $10^7\ M^{-1}\ \mathrm{sec}^{-1}$. Thus it was somewhat surprising to see a structure–rate correlation in these very fast reactions.

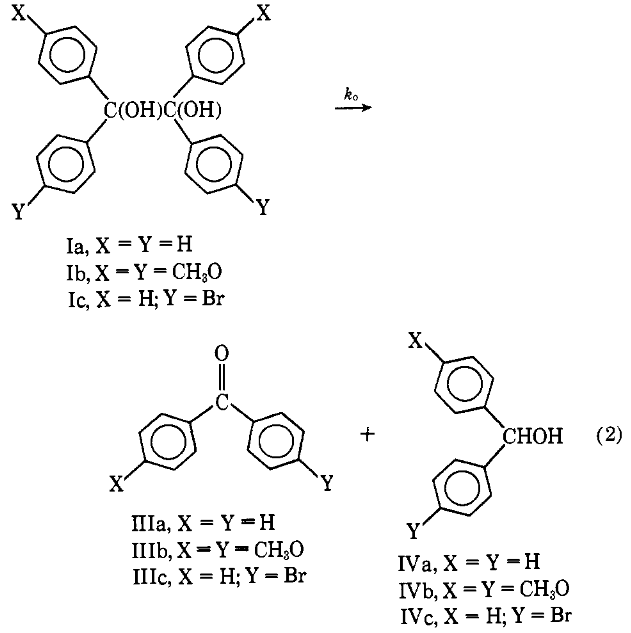
It was decided to see if this same structural correlation would appear in an equilibrium measurement. The equilibrium constants are obtained by combining the termination data with the rate constants for free radical production from the corresponding benzpinacols, k_s. While the thermal decomposition of benzpinacol, Ia, to yield benzophenone ketyl radicals, IIa, has been previously reported,[3–5] no thorough quantitative study has been done.[3,6] In this paper we report the results of the thermal decomposition of three benzpinacols in acetonitrile, benzene, and isopropyl alcohol solutions in the temperature range of 80–141°, and the activation energies for radical recombination.

Experimental Section

Materials. All solvents used were Matheson Coleman and Bell spectrograde. Benzene was stirred with concentrated sulfuric acid, separated, dried, and then distilled prior to use. Isopropyl alcohol was distilled from magnesium turnings. Acetonitrile was distilled from phosphorus pentoxide. Camphorquinone and benzpinacol were purchased from Aldrich Chemical Co. and were recrystallized from hexane and ethanol, respectively, prior to use. 4,4'-Dimethoxybenzophenone was chromatographed on alumina. 4-Bromobenzophenone was sublimed and then recrystallized from ethanol. 4,4',4'',4'''-Tetramethoxybenzpinacol (Ib) and 4,4''-dibromobenzpinacol (Ic) were synthesized by photolysis of the corresponding ketones in isopropyl alcohol. The resultant white solids were filtered and then recrystallized from ethanol. The quinone scavengers were used as received. All compounds had melting points in agreement with literature values.

Kinetic Measurements. All solutions were made up in cells shown in Figure 1 and were degassed by several freeze-pump-thaw cycles. The appearance of ketone and the disappearance of scavenger were monitored by absorption spectroscopy on a Cary recording spectrophotometer. Extinction coefficients for the compounds of interest measured on the same instrument are shown in Table I. The kinetic runs were done in a Blue M constant temperature bath using a thermocouple to check the bath temperature. At all settings used the bath temperature was constant to within ±0.2°.

In the absence of scavenger, the disappearance of benzpinacols (Ia,b,c) obeys eq 2.



Ia, X = Y = H
Ib, X = Y = CH_3O
Ic, X = H; Y = Br

IIIa, X = Y = H
IIIb, X = Y = CH_3O
IIIc, X = H; Y = Br

IVa, X = Y = H
IVb, X = Y = CH_3O
IVc, X = H; Y = Br

The data were plotted according to eq 3.

$$\ln\left((\mathrm{IIIa,b,c})_{t=\infty} - (\mathrm{IIIa,b,c})_t\right) = -k_0t + \ln(\mathrm{IIIa,b,c})_{t=\infty} \quad (3)$$

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[1] Presented in part at the 158th Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract PHYS 218.

[2] G. S. Hammond and S. A. Weiner, *Intra-Sci. Chem. Rep.*, **3**, 241 (1969).

[3] D. C. Neckers and D. P. Colenbrander, *Tetrahedron Lett.*, 5045 (1968).

[4] E. S. Huyser and D. C. Neckers, *J. Amer. Chem. Soc*, **85**, 3641 (1963).

[5] D. C. Neckers and A. P. Schaap, *J. Org. Chem.*, **32**, 22 (1967).

[6] G. O. Schenk, G. Matthias, M. Paper, M. Cziesla, and G. von Bünau published a study on the thermal decomposition of benzpinacol, Ia (*Justus Liebigs Ann. Chem.*, **719**, 80 (1968)), but unfortunately oxygen was used as the radical scavenger. When their conditions were duplicated, a $2.77 \times 10^{-3}\ M$ solution of Ia which was decomposed in xylene in the presence of oxygen had an absorbance of 1.13 at 342 nm while a $5.57 \times 10^{-3}\ M$ solution of benzophenone had an absorbance of 0.73 (ϵ 131 $M^{-1}\ \mathrm{cm}^{-1}$) at 343 nm in xylene. Essentially the same problem arose in dimethyl phthalate, chlorobenzene, and *n*-decane solutions. Furthermore, gpc analysis of the reaction mixtures showed several major products other than benzophenone.

Table I. Extinction Coefficients[a] at the Absorption Maxima

Compound	Solvent		
	Benzene	Isopropyl alcohol	Acetonitrile
Benzophenone	133.4	152.4	135.2
4-Bromobenzophenone	185.5	203.9	181.6
4,4′-Dimethoxybenzophenone	107,[b] 367[c]	46.0,[b] 423.4[c]	67.9,[b] 371.7[c]
Camphorquinone	38.3	39.9	39.2

[a] In units of M^{-1} cm^{-1} as measured on the instrument used for the kinetic runs. [b] Measured at 370 nm. [c] Measured at 350 nm.

A typical example of the data plotted in this manner is shown in Figure 2.

Substituted 1,4-benzoquinones and camphorquinone (V) proved to be good scavengers for the ketyl radicals.[7,8] Most of the work was done with camphorquinone as the scavenger as its absorption spectrum is such that the loss of camphorquinone and appearance of aromatic ketone can be monitored simultaneously. The results of a typical kinetic run are shown in Figure 3. In all cases, the rate constants for the appearance of aromatic ketone were independent of scavenger type and concentration. In the absence of scavenger, there was no induced decomposition of Ia,b,c. In fact, benzophenone ketyl radicals (IIa) will not abstract hydrogen atoms from 1,4-hydroquinones, dihydrocamphorquinone (VIa,b), isopropyl alcohol, and 1,4-cyclohexadiene. In the presence of scavenger, each mole of Ia,b,c essentially produces 2 mol of Va,b,c and no IVa,b,c (eq 4). The experimental ratios of IVa,b,c to Va,b,c

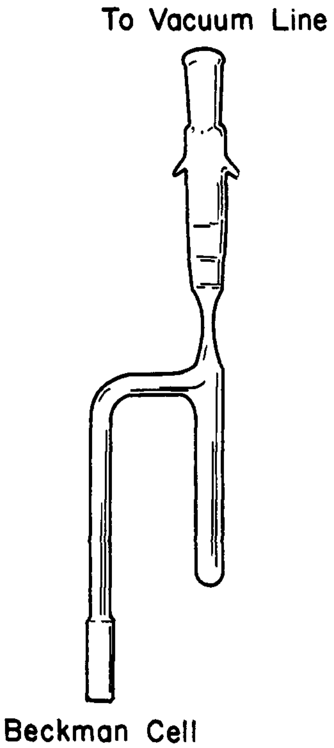
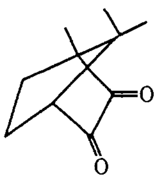
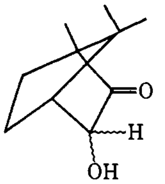


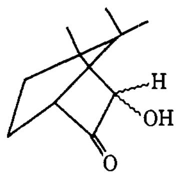
Figure 1. Illustration of cells used in the course of this work. In the evacuation procedure, the solution was kept in the cylindrical side arm. The solution was transferred to the Beckman cell when the absorption spectra were run.



V



VIa



VIb

$$\text{Ia,b,c} + \text{V} \xrightarrow{k_s} \text{VIa,b} + 2\text{IIIa,b,c} + \text{trace amounts of IVa,b,c} \quad (4)$$

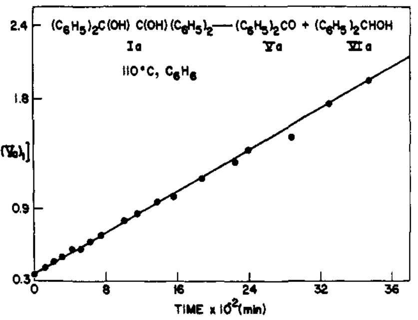


Figure 2. First-order plot for the decomposition of benzpinacol in benzene solution at 110° in the absence of scavenger. The data were plotted according to eq 3.

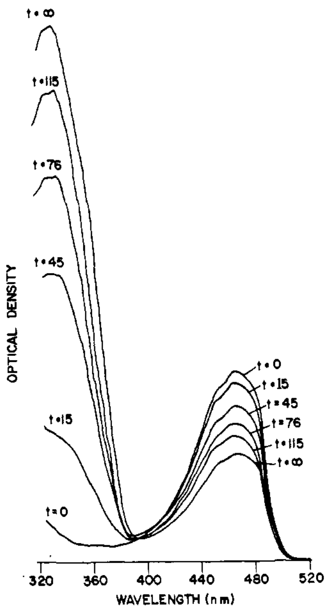


Figure 3. Absorption spectra taken during the course of the decomposition of 4,4′′′-dibromobenzpinacol (Ic) in benzene at 110° in the presence of camphorquinone. The peaks at 466 and 334 nm are due to camphorquinone and 4-bromobenzophenone, respectively.

in the presence of scavenger are on the order of 1 × 10^{-3}. Values of k_s are obtained from both the rate of appearance of ketone (eq 5)

$$\ln\left((\text{IIIa,b,c})_{t=\infty} - (\text{IIIa,b,c})_t\right) = -k_s t + \ln(\text{IIIa,b,c})_{t=\infty} \quad (5)$$

and the disappearance of camphorquinone (eq 6). The agreement

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[7] A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 67 (1944).

[8] B. M. Monroe and S. A. Weiner, *J. Amer. Chem. Soc.*, **91**, 450 (1969); S. A. Weiner, *ibid.*, **93**, 425 (1971).

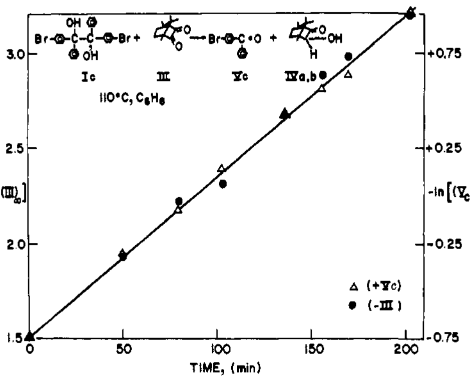


Figure 4. First-order plot for the decomposition of 4,4′′′-dibromobenzpinacol in benzene solution at 110° in the presence of camphorquinone. The data for appearance of 4-bromobenzophenone (Δ) were plotted according to eq 5. The data for disappearance of camphorquinone (○) were plotted according to eq 6

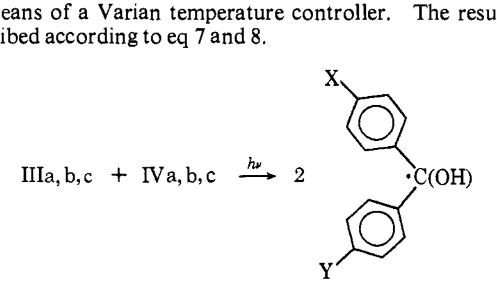
$$\ln\,[(\mathrm{V})_t - (\mathrm{V})_{t=\infty}] = -k_s t + \ln\,[(\mathrm{V})_{t=0} - (\mathrm{V})_{t=\infty}] \quad (6)$$

is quite satisfactory. Typical results are shown in Figure 4.

Product Analysis. After a minimum of 15 half-lives, the tubes were opened and the contents analyzed on a Beckman GC4 chromatograph with a logarithmic scale recorder and an Infotronics digital readout system, Model CRS-1145B/42. The columns used in this work were 1.5% Carbowax 20M on Gas Chrom Q, 1.5% Ucon-4B 2000 on Gas Chrom Q, and 1.5% polyphenyl ether on Gas Chrom T. The gpc data were calibrated by the use of standard solutions. On a few occasions, when the decomposition of 4,4′,4′′,4′′′-tetramethoxybenzpinacol was carried out in isopropyl alcohol, 4,4′-dimethoxybenzhydrol isopropyl ether was produced rather than the alcohol. In these cases, the gpc sensitivity was corrected by assuming that in the experiments without scavenger, the products were produced in a 1:1 ratio. Because of the low ratio of alcohol to ketone produced in the presence of scavenger, the experimental error associated with this number is on the order of ±20%. While the ratio of alcohol to ketone found was low, the alcohol could not have been present as an impurity in the starting benzpinacol as the ratio of alcohol to ketone varied by a factor of 4 as a function of solvent even though all the benzpinacol used was from the same batch.

Electron Spin Resonance (Esr) Experiments. Solutions of benzpinacols, Ia,b,c, in diphenyl ether were flushed with argon and placed in the cavity of a Varian E-3 esr spectrometer. The sample was heated to 141° by means of a Varian temperature controller. The intensity of the esr signal produced was measured relative to a standard containing manganese which was taped to the inside of the face plate. By calibrating the manganese standard with a standard weak pitch sample, absolute radical concentrations were obtained. These values have an error limit of ±50%.

Solutions of benzophenone, IIIa,b,c, and the corresponding benzhydrol, IVa,b,c, in benzene were flushed with argon and irradiated in the cavity of the esr spectrometer with light of wavelength greater than 330 nm. The temperature was varied from 30 to 73° by means of a Varian temperature controller. The results can be described according to eq 7 and 8.



$$\mathrm{IIIa,b,c} + \mathrm{IVa,b,c} \xrightarrow{h\nu} 2\ (\mathrm{XC_6H_4})(\mathrm{YC_6H_4})\dot{\mathrm{C}}(\mathrm{OH}) \quad (7)$$

IIa, X = Y = H
IIb, X = Y = CH_3O
IIc, X = H; Y = Br

$$2\mathrm{IIa,b,c} \xrightarrow{k_t} \mathrm{Ia,b,c} \quad (8)$$

Experimentally, it is observed that the radicals are at steady state. Thus we can equate the rate(s) of termination with the rate(s) of initiation. However, the rate of initiation is not a function of temperature but depends only on the light intensity, which is constant.[9] Thus the results may be interpreted in terms of eq 9 where

$$\Delta E_t/2.3RT = 2\log\,((\mathrm{IIa,b,c})_0{}^{T}/(\mathrm{IIa,b,c})_0{}^{T_1}) + \text{constant} \quad (9)$$

the superscript T refers to the temperature at which the measurements were made, T_1 = 30°, and the subscript 0 to the concentration at steady state. The same procedure was utilized in isopropyl alcohol solution except that the benzhydrol, IVa,b,c, was not added to the solution.

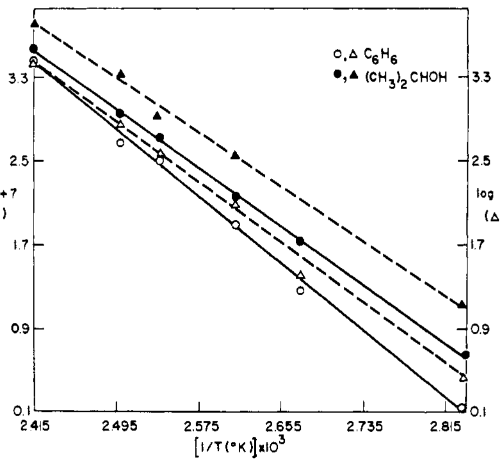


Figure 5. Plots of the first-order rate constants for the decomposition of benzpinacol in benzene solution in the absence (○) and presence (Δ) of scavenger and in isopropyl alcohol solution in the absence (●) and presence (▲) of scavenger *vs.* reciprocal temperature.

Results

Thermal Decomposition of Benzpinacols Ia,b,c. The results of the kinetic studies and product analyses from the thermal decomposition of benzpinacols Ia,b,c in benzene, acetonitrile, and isopropyl alcohol solutions are given in Table II. The rate constant k_0 refers to the decomposition in the absence of scavenger and k_s in the presence of scavenger. The values of k_s were obtained both from the rate of appearance of benzophenone, IIIa,b,c, and the rate of disappearance of scavenger. These values were independent of the particular scavenger used and the scavenger concentration. The ratio of benzhydrol, IVa,b,c, to benzophenone, IIIa,b,c, in the presence of scavenger is also reported in Table II. In the absence of scavenger, the ratio was 1:1. Activation energies and frequency factors for k_0 and k_s are given in Table III. Some Arrhenius plots are shown in Figure 5.

Temperature Dependence of the Rate Constant for Radical Termination. Using the technique described in the Experimental Section, the activation energies for termination of the ketyl radicals, IIa,b,c, have been determined. The results along with the previously reported values[2] of k_t at 30° are given in Table IV. Two examples of the Arrhenius plots are shown in Figure 6. It was not possible to make these measure-

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[9] This is so because the rate of initiation is equal to the rate of production of excited state provided that the excited state is completely quenched by the hydrogen donor. This criterion is met for the three ketones used in this study.[10]

[10] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965.

Table II. Rate Constants for the Disappearance of Benzpinacols Ia,b,c in the Absence (k_0) and Presence of Scavenger (k_s) and the Ratio of Benzhydrol, IVa,b,c, to Benzophenone, IIIa,b,c, in the Presence of Scavenger[a]

Benzpinacol $[(\mathrm{Ar})(\mathrm{Ar'})(\mathrm{OH})\mathrm{C}\text{–}_2]$	Temp, °C	Solvent								
		C_6H_6			$(CH_3)_2CHOH$			CH_3CN		
		$k_0 \times 10^7$, sec^{-1}	$k_s \times 10^6$, sec^{-1}	[IVa,b,c] $\times 10^3$/[IIIa,b,c]	$k_0 \times 10^7$, sec^{-1}	$k_s \times 10^6$, sec^{-1}	[IVa,b,c] $\times 10^3$/[IIIa,b,c]	$k_0 \times 10^7$, sec^{-1}	$k_s \times 10^6$, sec^{-1}	[IVa,b,c $\times 10^3$/[IIIa,b,c]
Ar = Ar' = C_6H_5 (Ia)	141	2970	2910	4.3	3840	5910	2.3	1950	3830	1.0
	127	458	701	5.4	880	2070	1.5	415	1160	1.2
	121	313	370	6.0	525	842	1.7	219	808	1.2
	110	75.8	123	3.9	141	347	0.8	58.2	222	0.4
	101	17.5	25.4	6.0						
	80	1.25	2.78	4.2	4.24	13.2	1.0			
Ar = Ar' = 4-$CH_3OC_6H_4$ (Ib)	141	1890	1040	19						
	127	370	226	30	980	744	24	662	710	25
	110	66.3	35.3	5.2	101	126	*b*	66.7	86.6	4.7
Ar = C_6H_5, Ar' = 4-BrC_6H_4 (Ic)	141	2030	3980	4.8						
	127	434	854	5.4	787	2570	2.8	535	1880	1.1
	121	251	514	4.9						
	110	79.6	145	2.9	133	575	0.5	70.5	328	1.1
	101	18.8	53.0	3.7						
	80	1.33	3.03	7.1	4.24	181	1.9			

[a] Determined by gpc. The error limit is ±20%. [b] Too low to determine.

Table III. Activation Energies and Frequency Factors for Reactions 2 and 4 as a Function of Solvent and Substituent

Benzpinacol	ΔE_{act}[a]			Log A[b]		
	C_6H_6	$(CH_3)_2CHOH$	CH_3CN	C_6H_6	$(CH_3)_2CHOH$	CH_3CH
			$\mathrm{Ia,b,c} \xrightarrow{k_0} \mathrm{IIIa,b,c,} + \mathrm{IVa,b,c}$			
Ia	36.8 ± 1.1	32.2 ± 0.9	35.4 ± 0.7	15.9 ± 0.6	13.6 ± 0.3	15.0 ± 0.4
Ib	33.6 ± 2.9	40.9[c]	41.4[c]	14.1 ± 1.6	18.4[c]	18.5[c]
Ic	34.8 ± 0.8	31.0 ± 1.0	36.5[c]	14.8 ± 0.4	12.9 ± 0.6	15.7[c]
			$\mathrm{Ia,b,c} + \mathrm{V} \xrightarrow{k_s} \mathrm{VIa,b,} + 2\mathrm{IIIa,b,c} + \text{trace IVa,b,c}$			
Ia	33.5 ± 1.2	27.3 ± 1.5	28.3 ± 1.9	15.2 ± 0.7	12.1 ± 0.9	12.4 ± 1.0
Ib	34.1 ± 0.9	32.0[c]	37.9[c]	15.1 ± 0.5	14.4[c]	17.6[c]
Ic	33.7 ± 0.5	29.7 ± 1.0	31.5[c]	15.5 ± 0.3	13.7 ± 0.6	14.1[c]

[a] The units are kcal/mol and the error limits are ± the standard deviation of the regression coefficient. [b] The error limits are ± the standard deviation of the regression coefficient. [c] Based on only two points.

Table IV. Arrhenius Parameters for the Rate Constant for Radical Termination, k_t

$$2\mathrm{IIa,b,c} \xrightarrow{k_t} \mathrm{Ia,b,c}$$

Radical	Solvent	k_t[a] $\times 10^{-8}$, M^{-1} sec^{-1}	ΔE_t,[b] kcal/mole	Log A_t
IIa	C_6H_6	18	1.0 ± 0.5	10.0
IIb	C_6H_6	63	−0.5 ± 0.5	9.5
IIc	C_6H_6	2.5	2.3 ± 0.3	10.1
IIa	$(CH_3)_2CHOH$	1.1	4.9 ± 0.3	11.6
IIc	$(CH_3)_2CHOH$	0.46	5.7 ± 0.3	11.8

[a] Values are taken from ref 2 and are at 30°. [b] The error limits are ± the standard deviation of the regression coefficient.

$$\underset{\mathrm{II}}{2(\mathrm{Ar})(\mathrm{Ar'})\dot{\mathrm{C}}(\mathrm{OH})} \xrightarrow{k_t} \underset{\mathrm{I}}{(\mathrm{Ar})(\mathrm{Ar'})\mathrm{C}(\mathrm{OH})\mathrm{C}(\mathrm{OH})(\mathrm{Ar})(\mathrm{Ar'})} \qquad (10)$$

a, Ar = Ar' = C_6H_5
b, Ar = Ar' = 4-$CH_3OC_6H_4$
c, Ar = C_6H_5; Ar' = 4-BrC_6H_4

ments in acetonitrile because of the high microwave absorptivity of that solvent. While the esr method does not distinguish between recombination and disproportionation as termination paths, it is well known that at room temperature recombination is dominant for these radicals.[4–6,10]

Measurement of the Equilibrium Constant at 141° in Diphenyl Ether Solution. Solutions of benzpinacols Ia,b,c in diphenyl ether at 141° produced measurable concentrations of benzophenone ketyl radicals, IIa,b,c. The radical concentrations did not vary over a period of 30 min. The equilibrium constants for Ib,c were

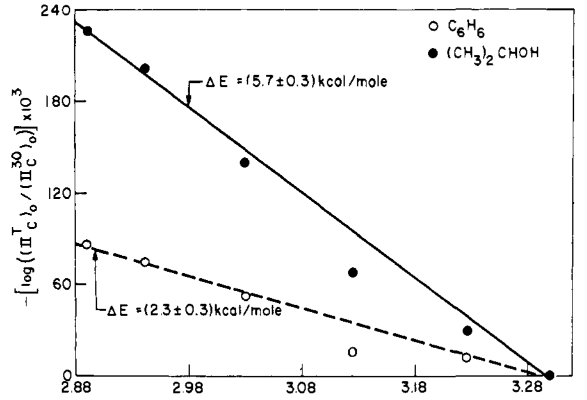

Figure 6. Plots of the logarithm of the relative concentration of 4-bromobenzophenone ketyl radical, IIc, in benzene (○) and isopropyl alcohol (●) solution *vs.* reciprocal temperature.

$$\mathrm{Ia,b,c} \overset{K_1}{\rightleftarrows} 2\mathrm{IIa,b,c} \qquad (11)$$

Table V. Equilibrium Constants, K_1, for Ia,b,c, $\rightleftarrows$ 2IIa,b,c in Diphenyl Ether at 141°

Radical	K_1(relative)	$K_1 \times 10^{12}$, M^a
$(C_6H_5)_2\dot{C}(OH)$ (IIa)	1.0	1.1
$(4\text{-}CH_3OC_6H_4)_2\dot{C}(OH)$ (IIb)	0.14	0.14
$(4\text{-}BrC_6H_4)(C_6H_5)\dot{C}(OH)$ (IIc)	11	11

[a] The values are correct to within a factor of 2.

Table VI. Thermodynamic Parameters for the Equilibrium Ia,b,c, $\rightleftarrows$ 2IIa,b,c along with Values of K_1 at 30° and 141°

Radical	Solvent	$K_1 \times 10^{12}$, M (141°)	$K_1 \times 10^{18}$, M (30°)	ΔH_1, kcal/mole	ΔS_1, eu
$(C_6H_5)_2\dot{C}(OH)$ (IIa)	C_6H_6	1.0	0.28	32.5 ± 1.7	23.9
	$(CH_3)_2CHOH$	4.7	120	22.4 ± 1.8	2.3
$(4\text{-}BrC_6H_4)(C_6H_5)\dot{C}(OH)$ (IIc)	C_6H_6	5.8	3.2	31.4 ± 0.8	23.9
	$(CH_3)_2CHOH$	17	350	24.0 ± 1.3	8.7
$(4\text{-}CH_3OC_6H_4)_2\dot{C}(OH)$ (IIb)	C_6H_6	0.10	0.16	34.5 ± 1.4	25.8

determined relative to Ia using eq 12. These

$$K_1^{b,c}/K_1^{a} = [(IIb,c)/(IIa)]^2[(Ia)/(Ib,c)] \qquad (12)$$

values are accurate to ±20%. The relative radical concentrations were converted to absolute values by the use of a previously calibrated standard weak pitch sample. The absolute values of the radical concentrations were then used to calculate absolute values of K_1 ($K_1^{a,b,c} = (IIa,b,c)^2/(Ia,b,c)$). Because these values of K_1 depend on the square of the radical concentration they are accurate only within a factor of 2. The results are given in Table V.

Discussion

Equilibrium Constants. The equilibrium constants (K_1) for dissociation of the benzpinacols Ia,b,c to a pair of free benzophenone ketyl radicals IIa,b,c is just equal to k_s/k_t where k_s is the rate constant for production of radicals from the benzpinacol and k_t that for termination of the radicals to produce benzpinacol. These values are independent of the choice of reaction scheme but are correct only to the extent that k_t represents the true value for radical recombination. While it is well known that recombination is the major if not the exclusive path for termination at room temperature,[10] results from this study and earlier work[4-6] show that this is still true at 141°. Use of the relationship $K_1 = k_s/k_t$ leads to eq 13 and 14. The values

$$\Delta H_1 = \Delta E_s - \Delta E_t \qquad (13)$$

$$\Delta S_1 = 2.3R(\log A_s - \log A_t) \qquad (14)$$

of ΔH_1 and ΔS_1 are given in Table VI along with values of K_1 at 141° and 30°.

The agreement between the values of K_1 at 141° in benzene and diphenyl ether is good. The results also show that isopropyl alcohol shifts the equilibrium to the radical side relative to the two aromatic solvents. The equilibrium constants in benzene and diphenyl ether show that radical stability lies in the order IIc > IIa > IIb. The termination constants, k_t, were in the order IIb > IIa > IIc.[2] Thus for these ketyl radicals, the more stable radical undergoes termination more slowly. This agreement between radical termination rates and radical stability is not always obtained.[11,12] Furthermore the rate constant for radical production, k_s, lies in the order IIc > IIa > IIb in benzene solution at all temperatures studied. Using k_s to determine radical stability in isopropyl alcohol and acetonitrile leads to the result that in these solvents as well stability lies in the order IIc > IIa > IIb. In fact, the equilibrium constant shows that IIc is more stable than IIa in isopropyl alcohol. Assuming that ΔE_t in acetonitrile is small, then $\Delta H_1 \leq \Delta E_s$. For radical IIa, $(C_6H_5)_2\dot{C}(OH)$, this places an upper limit of 28.3 ± 1.9 kcal/mol on ΔH_1. Thus for IIa, acetonitrile appears to lie between benzene and isopropyl alcohol as a solvent. Also, the effect of remote substituents is much smaller than the effect of solvent.

In going from benzene to isopropyl alcohol solution at 30°, K_1 increases by a factor of 430 for $(C_6H_5)_2\dot{C}(OH)$, IIa. The heats of solution at high dilution of benzpinacol, Ia, in benzene and isopropyl alcohol are 3.8 ± 0.2 and 4.2 ± 0.3 kcal/mol, respectively.[13] Therefore the large change in K_1 must be associated with the increased solvation of the radical by isopropyl alcohol relative to benzene rather than with solvation of the parent benzpinacol. Using the values of ΔH_1 together with the heats of solution of benzpinacol, the transfer of a benzophenone ketyl radical IIa, at high dilution, from benzene to isopropyl alcohol solution, is

$$IIa(C_6H_6) \longrightarrow IIa((CH_3)_2CHOH)$$

exothermic by 5 ± 2 kcal/mol. This value is similar to the heat corresponding to the transfer of an alcohol in a state of high dilution in benzene to pure liquid alcohol.[14] Moreover, the value of $\Delta(\Delta S_1)$ for the transfer of a benzophenone ketyl radical from benzene to isopropyl alcohol, 10.8 eu, is also similar to the values observed for formation of a hydrogen bond of O-H with oxygen containing acceptor molecules.[14]

Mechanism of the Decomposition. The kinetic results and product studies are best accommodated by the following scheme where overlines indicate caged radical pairs and camphorquinone, V, is used as the scavenger.

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

(12) R. D. Burkhart, *ibid.*, **90**, 273 (1968).

(13) Measured in this laboratory by J. Chen. See L. R. Mahoney, F. C. Ferris, and M. A. DaRooge, *J. Amer. Chem. Soc.*, **91**, 3883 (1969), for details.

(14) E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie, and P. v. R. Schleyer, *ibid.*, **92**, 2365 (1970), report that the heat of solution of *n*-butyl alcohol in benzene is endothermic by 3.93 ± 0.08 kcal/mol.

Table VII. The Fraction of Cage Reaction, a, the Rate Constant for Cage Formation from Benzpinacol, k_{clev}, and the Ratio of Recombination to Disproportionation, k_{rec}/k_{dis}

Radical $[(Ar)(Ar')\dot{C}(OH)]$	Temp, °C	Solvent								
		C_6H_6			$(CH_3)_2CHOH$			CH_3CN		
		a	$k_{clev} \times 10^6$, sec^{-1}	k_{rec}/k_{dis}	a	$k_{clev} \times 10^6$, sec^{-1}	k_{rec}/k_{dis}	a	$k_{clev} \times 10^6$, sec^{-1}	k_{rec}/k_{dis}
Ar = Ar' = C_6H_5	141	0.08	3170	9.7	0.07	6350	16	0.04	3990	20
(IIa)	127	0.17	845	17	0.07	2230	24	0.06	1230	29
	121	0.14	430	13	0.05	886	16	0.09	888	40
	110	0.13	140	17	0.04	363	25	0.03	229	38
	101	0.17	30.6	16						
	80	0.19	3.43	26	0.06	15.0	34			
Ar = Ar' = 4-$CH_3OC_6H_4$	141	0.21	1320	6.0						
(IIb)	127	0.36	350	8.5	0.36	1160	11	0.49	1390	20
	110	0.06	37.6	4.7				0.12	98.4	14
Ar = C_6H_5, Ar' = 4-BrC_6H_4	141	0.19	4910	23						
(IIc)	127	0.21	1080	24	0.18	3130	39			
	121	0.20	643	25						
	110	0.10	159	19	0.04	599	33	0.08	2040	37
	101	0.20	67.1	35						
	80	0.32	4.47	33	0.16	21.5	50	0.10	364	51

$$(Ar)(Ar')C(OH)C(OH)(Ar)(Ar') \underset{k_{rec}}{\overset{k_{clev}}{\rightleftarrows}} \overline{2(Ar)(Ar')\dot{C}(OH)} \quad (15)$$

Ia, Ar = Ar' = C_6H_5 IIa, Ar = Ar' = C_6H_5
Ib, Ar = Ar' = 4-$CH_3OC_6H_4$ IIb, Ar = Ar' = 4-$CH_3OC_6H_4$
Ic, Ar = C_6H_5; Ar' = 4-BrC_6H_4 IIc, Ar = C_6H_5; Ar' = 4-BrC_6H_4

$$\overline{2\text{IIa,b,c}} \xrightarrow{k_{dis}} \underset{\text{IIIa,b,c}}{(Ar)(Ar')C{=}O} + \underset{\text{IVa,b,c}}{(Ar)(Ar')CHOH} \quad (16)$$

$$\overline{2\text{IIa,b,c}} \underset{k_D}{\overset{k_d}{\rightleftarrows}} 2\text{IIa,b,c (free)} \quad (17)$$

$$2\text{IIa,b,c(free)} + \text{camphorquinone} \xrightarrow{\text{fast}} 2\text{IIIa,b,c} + \text{dihydrocamphorquinone} \quad (18)$$

The second-order bulk encounter constant is represented by k_D while k_d is the first-order rate constant for diffusive destruction of the radical cage. In the presence of scavenger, the free radicals IIa,b,c are trapped before they can reform a caged pair of radicals. This scheme differs from that of previous workers[3,6] only in the inclusion of cage reactions. However, a cage reaction must be included because benzhydrols, IVa,b,c are produced in the presence of scavenger. The scavengers used oxidize the radicals to benzophenones. Furthermore, the ratio of benzhydrol to benzophenone in the presence of scavenger was independent of the scavenger concentration.

Estimation of the Fraction of Cage Reaction, a. Steady-state analysis of the reaction scheme leads to eq 19 expressing a, the fraction of cage reaction, in

$$a = \text{fraction of cage reaction} = 2(k_s/k_0)((\text{IVa,b,c})/(\text{IIIa,b,c})) \quad (19)$$

terms of the three experimentally measured quantities.[15] The error limits for a are ±30%. The values of a are listed in Table VII. Within experimental error, a is approximately 0.2 for all three ketyl radicals in benzene solution independent of temperature. If we limit the discussion in isopropyl alcohol and acetonitrile solutions to radicals IIa,c, then there is no discernible effect on a of temperature variation. However the value of a is approximately 0.07 for $(C_6H_5)_2\dot{C}(OH)$, IIa, and 0.1 for $(C_6H_5)(4\text{-}BrC_6H_4)\dot{C}(OH)$, IIc, in both solvents. The value of 0.07 in isopropyl alcohol is close to that reported for IIa and acetone ketyl in this solvent.[8] In summary, a appears to be lower in isopropyl alcohol and acetonitrile than in benzene but in no case was $a = 0$. On the other hand a is much less than unity for any of these radicals.

The Ratio of Recombination to Disproportionation, k_{rec}/k_{dis}. Analysis of reactions 15–17 leads to eq 20

$$k_{rec}/k_{dis} = (k_s/(1 - a) - k_0)/k_0 \quad (20)$$

relating the ratio of recombination to disproportionation to k_0, k_s, and a.[15] Values of k_{rec}/k_{dis} are listed in Table VII. While there is considerable scatter in these values, they are all greater than 10. This justifies the earlier assumption that termination proceeds predominantly *via* recombination. There is a tendency for k_{rec}/k_{dis} to increase with decreasing temperature.[16] Earlier workers had reported that this ratio is constant for benzophenone ketyl radical, IIa, in benzene.[6]

In general, the values of k_{rec}/k_{dis} are higher in isopropyl alcohol and acetonitrile than in benzene. This is consistent with the formation of a hydrogen bond between the ketyl radicals (donors) and the former two solvents (acceptors). Finally, in all three solvents, the ratio of recombination to disproportionation parallels radical stability; *i.e.*, the most stable radical is the least likely to disproportionate.

On the Activation Energy for Radical Termination, ΔE_t. In terms of the reaction scheme (eq 15–17), k_t =

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(15) This relationship is derived by algebraic manipulations of eq i–iii which express the experimentally determined parameters in terms of the rate constants for reactions 15–17.

$$k_0 = k_{clev}k_{dis}/(k_{dis} + k_{rec}) \quad \text{(i)}$$

$$k_s = k_{clev}k_d/(k_{dis} + k_{rec} + k_d) = (k_{clev})(1 - a) \quad \text{(ii)}$$

$$(\text{IVa,b,c})/(\text{IIIa,b,c}) = k_{dis}/2k_d \quad \text{(iii)}$$

(16) This conclusion is supported by the following analysis. For $a \ll 1$, and $k_{rec}/k_{dis} \gg 1$, both of which are true here, the ratio of recombination to disproportion is approximated by k_s/k_0. This leads to eq iv. An examination of Table III reveals that in general ΔE_0 is greater

$$\Delta E_{rec} - \Delta E_{dis} = \Delta E_s - \Delta E_0 \quad \text{(iv)}$$

than ΔE_s by at least 1 kcal/mol. Thus $\Delta E_{rec} - \Delta E_{dis} < 0$ and therefore the ratio of recombination to disproportionation should increase with decreasing temperature.

Table VIII. Experimental and Calculated Values of k_D at 80°

Radical	Solvent	$k_D = (k_t/a) \times 10^{-8}$, M^{-1} sec^{-1}	$k_D = (8RT/3000\,\eta) \times 10^{-8}$, M^{-1} sec^{-1}
$(C_6H_5)_2\dot{C}(OH)$	C_6H_6	120	240
(IIa)	$(CH_3)_2CHOH$	58	140
$(C_6H_5)(4\text{-}BrC_6H_4)\dot{C}(OH)$	C_6H_6	13	240
(IIc)	$(CH_3)_2CHOH$	11	140

ak_D where k_D is the bulk encounter constant. This leads to eq 21. Under our conditions ΔE_a was ap-

$$\Delta E_t = \Delta E_a + \Delta_D \tag{21}$$

proximately zero. However in principle ΔE_a should be negative provided a is less than one[17] leading to $\Delta E_t \leq \Delta E_D$. Estimates of ΔE_D are 2.9 kcal/mol in benzene and 6.4 kcal/mol in isopropyl alcohol.[19-21] These values are obtained by use of the modified Debye equation, $k_D = 8RT/3000\eta$, where η is the solvent viscosity.[21] Examination of the values of ΔE_t in Table IV shows that the inequality, $\Delta E_t < \Delta E_D$, is obeyed.

One can use the relation $k_t = ak_D$ to obtain values of k_D. These values are compared with those calculated from the modified Debye equation in Table VIII. The agreement is good for $(C_6H_5)_2\dot{C}(OH)$ but the effect of the bromo substituent is much larger than what is expected on the basis of simple diffusion theory.

Summary

In isopropyl alcohol (and probably acetonitrile) the ketyl radicals are hydrogen bonded to the solvent. This hydrogen bonding accounts for the shift of the equilibrium (Ia,b,c $\rightleftarrows$ 2IIa,b,c) to the radical side on going from benzene to isopropyl alcohol solution. The order of radical stability as determined by the equilibrium constant, K_1, also appears in the rate constants for cleavage of the benzpinacols and those for termination of the ketyl radicals. This order is reflected in the ratio of recombination to disproportionation, the most stable radical being the least likely to disproportionate. While the effect of remote substituent is much smaller than that of solvent, the ketyl radical is stabilized by replacement of a para hydrogen by bromine and destabilized by replacement with a methoxy group.

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[17] This is so because as the temperature decreases, the solution viscosity increases and it is well known that at a fixed temperature a increases with increasing viscosity.[16]

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Transmission of Substituent Effects in Anthracene. Acid Dissociation Constants of 10-Substituted-9-anthroic Acids and Substituent Chemical Shifts of 10-Substituted-9-fluoroanthracenes. Evidence for the π Inductive Effect[1]

Gloria L. Anderson, Roger C. Parish, and Leon M. Stock*

Contribution from the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. *Received January 30, 1971*

Abstract: The acid dissociation constants for six 10-substituted-9-anthroic acids have been determined for 50% aqueous ethanol. The substituent chemical shifts for 14 10-substituted-9-fluoroanthracenes have been determined for six solvents. The results support the view that substituent effects propagated by π electron interactions, in particular π induction, are enhanced in the meso anthracenes relative to the para benzenes.

Four component interactions are often considered in discussions of the propagation and transmission of the electronic effects of substituent groups.[2,3] These interactions are designated as the polar (inductive) effect, the π inductive (inductoelectromeric or inductomesomeric) effect, the resonance (mesomeric) effect, and the direct conjugative (electromeric) effect.[2,3] It is now well recognized that progress in the definition of the factors governing the propagation of substituent effects and in the development of satisfactory empirical and theoretical methods for the treatment of substituent effects requires the investigation of carefully selected model compounds in which the capacity for the transmission of the electronic effects may be varied systematically. Thus, the study of substituent effects in rigid bicyclic molecules, initiated by Roberts and Moreland, has enabled the definition of the magnitude of monopolar and dipolar substituent effects for selected, fixed geometries and

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