line 3_1 helical poly(n-butene-1) is 17.7 Å,[43] which corresponds to the width of two molecules. The shifts in helix axes required by both conformations i and ii are small by comparison. Either presumably could be accommodated without excessive distortion of the crystal. Moreover, the calculated displacements of the helix axis may be diminished by compromising bond rotation angles from those stipulated above.

Conformation i entails a smaller displacement of axis but requires a commitment of several kilocalories per mole. The enthalpy of fusion of isotactic poly(n-butene-1) is about 1500 cal/mole of C_4 units.[36,37] Even the presence of one syndiotactic unit in ten would appropriate only about one-fifth of the molar heat of fusion for an isotactic sequence of average length. Conformation ii does not require a contribution to the intramolecular energy, but it involves a larger "fault" in the crystal.

The reversal of helix screw sense at each interruption of a succession of isotactic units by a syndiotactic unit implies that the senses of rotation of neighboring chains in the crystal lattice must be random. Only in this respect is the present interpretation at variance with the structures proposed for crystalline isotactic polymers by Natta, Corradini, and their co-workers[34,43] on the basis of their pioneering investigations. They considered neighboring chains to be enantiomorphous, *i.e.*, of opposite helical screw sense. On the other hand, they concluded that oppositely directed helices of a given screw sense (*i.e.*, g^+t and tg^+ for right-handed and tg^- and g^-t for left-handed helices) probably locate at random in the crystal, their directions thus being essentially uncorrelated with those of their neighbors. Placement of all R groups of neighboring helices at the same level in the crystal then requires corresponding (random) axial translations of the helices by distances of one bond length. Skeletal bonds of neighboring bonds are not then in register.

It is worthy of note that both isotactic and syndiotactic poly(methyl methacrylate) are highly crystalline despite the presence of *ca.* 20% of heterotactic units in each.[44,45] The possibility of accommodating heterotactic units within the crystalline phase was pointed out long ago by Bunn and Peiser.[46]

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF49(638)-1341.

(43) G. Natta, P. Corradini, and I. W. Bassi, *Nuovo Cimento, Suppl.*, **15**, 52, 68 (1960).

(44) F. A. Bovey and G. V. D. Tiers, *J. Polymer Sci.*, **44**, 173 (1960).

(45) D. Braun, M. Herner, U. Johnsen, and W. Kern, *Makromol. Chem.*, **51**, 15 (1962); U. Johnsen, *Kolloid-Z.*, **178**, 161 (1961).

(46) C. W. Bunn and H. S. Peiser, *Nature*, **159**, 161 (1947); C. W. Bunn, *ibid.*, **161**, 929 (1948).

The Thermochemistry of the Gas Phase Equilibrium $I_2 + C_6H_5CH_3 \rightleftarrows C_6H_5CH_2I + HI$ and the Heat of Formation of the Benzyl Radical[1]

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Abstract: With the aid of a Cary spectrophotometer, modified for use with high-temperature gas systems, the equilibrium constant for the reaction $C_6H_5CH_3 + I_2 \rightleftarrows C_6H_5CH_2I + HI$ has been measured over the temperature range 210–390°. From a plot of log K_{eq} against $1/T$(°K), the following thermodynamic values were calculated: $\Delta H°_{573} = +10.30 \pm 0.17$ kcal/mole and $\Delta S°_{573} = 2.65 \pm 0.27$ gibbs/mole. When corrected to room temperature using an independent estimate of $\overline{\Delta C_p}° = 1.6 \pm 1.0$ gibbs/mole, these become: $\Delta H°_{298} = +9.86 \pm 0.32$ kcal/mole and $\Delta S°_{298} = +1.59 \pm 0.71$ gibbs/mole. This latter is in excellent agreement with an independent estimate based on bond additivity of $+1.0 \pm 1.0$ gibbs/mole, and the former, when combined with known values[2] of the heats of formation of $C_6H_5CH_3$, HI, and I_2, yields a value for $\Delta H_f°(C_6H_5CH_2I(g))$ of $+30.43 \pm 0.32$ kcal/mole. Crude kinetic data were also obtained within the temperature range 210–270°. Assuming the rate-controlling step in the initial stages of reaction to be that shown in eq ii in the text the following Arrhenius parameters were calculated: $\log k_4 = 8.43 \pm 1.22 - (14.4 \mp 2.9)/\theta$. From this activation energy, and an assumed value of $E_3 = 1.5$ kcal/mole, it may be shown that $\Delta H_f°(C_6H_5CH_2\cdot(g)) = 44.1 \pm 3.1$ kcal/mole and $DH°_{298}(C_6H_5CH_2\text{–}H) = 84.2 \pm 3.1$ kcal/mole, in good agreement with values from recent kinetic studies.

Using a spectrophotometric technique, it has been shown[3] that the kinetic parameters and equilibrium constants of reactions of the type $RH + I_2 \rightleftarrows RI + HI$ may be conveniently and accurately determined in the temperature range 200–400°, even though the extent of reaction is small and the equilibria are well to the left. We have previously used the technique[3] to obtain an accurate value for $\Delta H_f°(CH_3I(g))$ and to

(1) This investigation was supported in part by Public Health Service Research Grant AP-00353-01 from the Air Pollution Division, Public Health Service.

(2) (a) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Carnegie Press, Pittsburgh, Pa., 1953; (b) "JANAF Interim Thermochemical Tables," D. R. Stull, Ed., Dow Chemical Co. Midland, Mich., 1963.

(3) D. M. Golden, R. Walsh, and S. W. Benson, *J. Am. Chem. Soc.*, **87**, 4053 (1965).

redetermine the important quantity $\Delta H_f°(CH_3(g))$. The work presented here represents an extension of these studies to the case where R = $C_6H_5CH_2\cdot$. This case is very important because of the controversy over the resonance energy associated with the benzyl radical. A wealth of measurements of the quantity $\Delta H_f°(C_6H_5CH_2\cdot(g))$ and the associated $DH°_{298}(C_6H_5CH_3\text{–}H)$ exist. Benson and Buss,[4] Sehon and Szwarc,[5] Trotman-Dickenson and co-workers,[6] and Skinner[7] have all reviewed the subject, and while values for $\Delta H_f°(C_6H_5CH_2(g))$ all appear to lie within the range 38–46.5 kcal/mole [implying $DH°_{298}(C_6H_5CH_2\text{–}H)$ lies between 78 and 86.5 kcal/mole] there is no general agreement on a precise value.

Experimental Section

Materials. Baker and Adamson reagent grade toluene was used, fresh samples being taken from the bottle and thoroughly degassed before each run. This was to avoid saturating the silicone grease of the stopcocks in the system with toluene, and also, as far as possible, to avoid contamination of the toluene with grease. Reagent grade resublimed iodine was used. Matheson anhydrous hydrogen iodide and Eastman benzyl iodide were both purified by vacuum distillation, the latter (a solid) requiring to be washed free of iodine with liquid toluene beforehand (the toluene was removed by subsequent distillation).

Apparatus. The apparatus has been described in detail previously.[3] The spectrophotometric sensitivity toward benzyl iodide was found to be such as to permit detection of 10^{-4} torr or $\sim 3 \times 10^{-9}$ mole/l. at our temperatures.

Procedure. Examination of the ultraviolet spectra of toluene and benzyl iodide suggested that the present reaction would be most conveniently monitored at a wavelength of 235 mμ. At this wavelength the benzyl iodide spectrum was found to be more than 30 times as intense as that of HI, the next strongest absorber. Accordingly changes, which were always increases, in absorbance at 235 mμ during the reaction could be almost unambiguously attributed to benzyl iodide formation, once it was verified that no side reactions were occurring. In practice, it was found necessary to suppress the formation of benzyl iodide, because of its thermal instability at some of the temperatures used in this work, by addition of extra HI to the system. Thus typical equilibrium pressures of benzyl iodide lay in the range 10^{-1}–10^{-2} torr, which were nevertheless easily measured.

The procedure for an individual run was as follows. The absorbance of the empty cell (evacuated to 10^{-5} torr) was recorded at 235 and 350 mμ (this latter wavelength proved to be an optical window for the system and therefore served as a convenient reference point). HI (when required), I_2, and $C_6H_5CH_3$ were successively metered into the vessel (usually in the order stated but not always so), their pressures being determined in turn by means of a pressure transducer nulled with air. After addition of each successive gas, the absorbance at 235 mμ was recorded and the absorbance of the system was then observed from time to time until no further change occurred, at which point it was presumed that the equilibrium had been established. The increase in absorbance due to reaction was then measured and converted by means of a previous calibration for benzyl iodide (corrected to allow for small changes in I_2, $C_6H_5CH_3$, and HI) into a final pressure for benzyl iodide. This pressure was then added to that of HI and subtracted from those of $C_6H_5CH_3$ and I_2 to obtain equilibrium pressures of these three components. The equilibrium constant was then simply evaluated.

At higher temperatures, equilibrium was established almost instantaneously, and it was not possible to separate absorbance due to addition of toluene from absorbance resulting from reaction. It was therefore necessary to calibrate for toluene rather carefully. This was done at all temperatures employed in this work, and the absorbance was always found to obey Beer's law within better than 1%, although the variation of absorptivity (= absorption coefficient[8] × path length) with $1/T$(°K), shown in Figure 1b, is somewhat unusual.[8] By contrast with this behavior, calibrations for benzyl iodide not only obeyed Beer's law but the absorptivity varied linearly with $1/T$ as can also be seen from Figure 1a. This result was important because it was not possible to calibrate for benzyl iodide above 300° (because of its instability), but its sensitivity could be obtained by a linear extrapolation of the low-temperature plot.

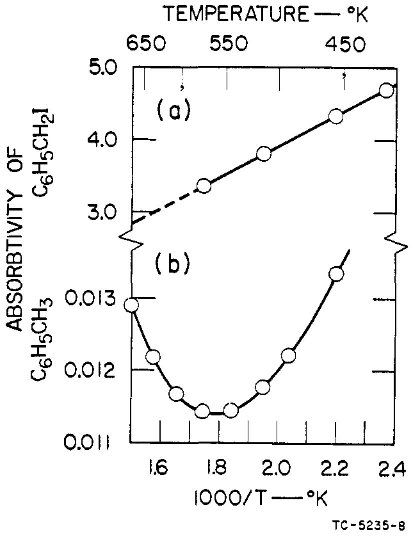

Figure 1. Plot showing the variation of spectrophotometric sensitivity (or absorptivity) of the system toward toluene and benzyl iodide with temperature (for units of absorptivity, see text and ref 8). Note: Each point marked ○ on this graph represents a separate check (involving three or four measurements of both pressure and absorbance) of Beer's law; in a, the dashed portion of the graph represents the assumed extrapolation (all absorbtivities at 235mμ).

In some runs, an established equilibrium was pressurized with more $C_6H_5CH_3$ and, in other cases, HI, and then permitted to reach a new equilibrium. The calculation was then performed as before. In addition iodine was occasionally monitored, for checking purposes, at 500 mμ where it is the only absorbing species.

For the kinetic measurements the procedure for an individual run was similar except that a stopwatch was started when the toluene was added to reaction mixture and the spectrophotometer recorder chart was left running in order to record continuously the changes in absorbance at 235 mμ. (It was verified several times that the reaction rate was unaffected by light from the spectrometer.) From the slope of the resulting trace and the rate of recorder chart feed out, the initial rate of absorbance increase was calculated. By means of the calibrations, already mentioned, this was converted to an initial rate of benzyl iodide formation. During the course of this work the silicone grease of the heated stopcock isolating the reaction vessel was changed from silicone (Dow-Corning) to Apiezon H, and back. No effect on the results was observed, and it could therefore be presumed that the system was unaffected by grease.

Results

Equilibrium Measurements. Preliminary experiments without added HI gave rather a wide scatter in values for the equilibrium constant, but this was considerably improved when HI was added. Furthermore, it was found that experiments with high pressures of iodine and low pressures of toluene tended to give low values for the equilibrium constant; however, provided extremely low values for the ratio $[C_6H_5CH_3]/[I_2]$ were

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(4) S. W. Benson and J. H. Buss, *J. Phys. Chem.*, **61**, 104 (1957).

(5) A. H. Sehon and M. Szwarc, *Ann. Rev. Phys. Chem.*, **8**, 445 (1957).

(6) G. L. Esteban, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3873 (1963).

(7) H. A. Skinner, *Ann. Rev. Phys. Chem.*, **15**, 461 (1964).

(8) The absorption coefficient, α_p, used here is defined by the following equation: $\log (I_0/I) = \alpha_p pl$, where p is the pressure in torr, and l the path length in cm. Because α_p is measured in pressure units, it is related to α_c, measured in concentration units, by $\alpha_c = \alpha_p RT$. Thus if α_c is independent of temperature (this is true for many molecules over substantial wavelength regions), α_p should be a linear function of $1/T$(°K).

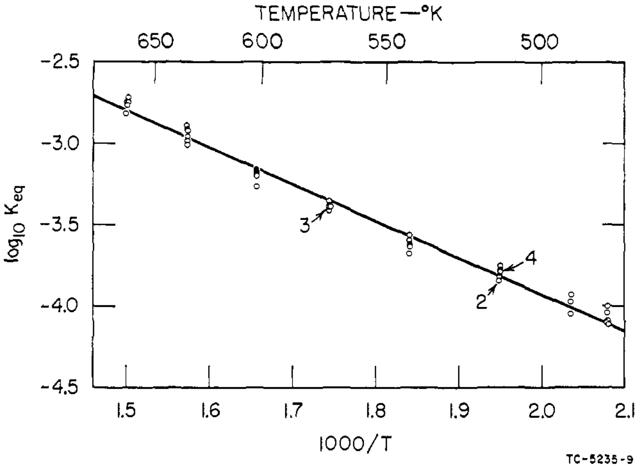

Figure 2. van't Hoff isochore plots of the equilibrium constant for $I_2 + C_6H_5CH_3 \rightleftharpoons C_6H_5CHI + HI$ (numbers indicate number of overlapping points).

avoided, it was possible to obtain good constancy for a wide variety of initial conditions. Benzyl iodide alone was found to be stable at the low pressures employed in this work below 270°, and while unstable above this temperature its rate of decomposition was considerably retarded in the presence of either $C_6H_5CH_3$ or I_2. In view of these uncertainties, a number of independent checks on the system were made. First, overall pressure was observed at equilibrium in a number of runs and was always found to have remained constant within ±0.6 torr during reaction. Second, spot checks on the iodine consumed during the reaction were always equal to the benzyl iodide formed within experimental error. Although this was generally not a very sensitive test because of the small values of the equilibrium constant, in two runs with no original HI, but with a high ratio of $[C_6H_5CH_3]/[I_2]$, a reasonable per cent of iodine conversion was achieved and an accurate iodine balance was also obtained. All these results indicated that no gross side reaction was occurring. The possibility that the iodide product was not benzyl iodide, but one of its isomers, can also be rejected as a result of these observations, since *o*-, *m*-, and *p*-tolyl iodides (the remaining aromatic possibilities for C_7H_7I) all have considerably lower absorptivities at 235 mμ and, if formed, would require a considerably greater conversion of iodine than was observed.

Third, an ultraviolet scan of one equilibrium mixture at 240° showed good semiquantitative agreement with that calculated by summation of spectra of the individual components.

Fourth and most convincingly, the range of values of $[C_6H_5CH_3]/[I_2]$ was varied by more than a factor of 50 at all temperatures. On two occasions the equilibrium was established from the reverse direction by pressurizing a previous equilibrium mixtue with HI.

In view of the recently measured equilibrium[9]

$$I_2 + C_6H_6 \rightleftharpoons \text{charge-transfer complex}$$

the possibility of a similar complex of iodine with toluene cannot be overlooked. However, if such a complex were formed, its absorbance under the lower temperature conditions employed here is certainly small since addition of toluene to iodine initially gives a mixture whose absorbance is the simple sum, within experimental error, of the individual absorbances (that is, before benzyl iodide begins to be formed), and a complex would certainly be formed instantaneously. At higher temperatures such a complex would be even more unstable.

The detailed results of the equilibrium measurements are listed in Table I; the subscript "0" refers to initial pressures while "eq" stands for equilibrium quantities. Only the directly measured equilibrium pressure of benzyl iodide is listed, but other equilibrium pressures may be readily obtained by substraction. Some measurements were attempted at 150 and 180° but these were very irreproducible and are therefore not included here. However, the temperature range 207–393° is substantial, and although benzyl iodide alone is unstable at the higher temperatures of this work, it was felt that the achievement of a steady state of absorbance coupled with reasonable reproducibility of equilibrium constants guarantees the stability of the small quantities of benzyl iodide produced in this system.

These data are exhibited in Figure 2 in the form of a plot of the Van't Hoff isochore equation showing a good linear fit over the entire range. A least-mean-square treatment of these data yielded (from the computed slope and intercept): $\Delta H°_{573} = +10.30 \pm 0.17$ kcal/mole and $\Delta S°_{573} = +2.65 \pm 0.57$ gibbs/mole. The high accuracy of these figures is a consequence of the wide temperature range of the measurements. The errors quoted are standard errors.

In order to compare these values with other work, they were corrected to room temperature using $\overline{\Delta C_p}° = +1.60 \pm 1.0$ gibbs/mole. This figure was calculated from known values of $C_p°$ for HI and I_2 and an estimate of the difference $C_p°(\text{R–I}) - C_p°(\text{R–H})$ based on differences for compounds whose $C_p°$ values are known,[10] within the temperature range 298–573°.

The room temperature values are $\Delta H°_{298} = +9.86 \pm 0.32$ kcal/mole and $\Delta S°_{298} = +1.59 \pm 0.71$ gibbs/mole. The entropy value is in very good agreement with a calculation we have made based on bond additivity,[11] which gives $\Delta S°_{298} = 1.00 \pm 1.0$ gibb/mole. The individual entropies and data sources are listed in Table II. The error attached to this value is based on the experience that bond additivity predictions are usually reliable to better than ±1.0 gibbs/mole.

The value for the heat change may be used to evaluate $\Delta H_f°(C_6H_5CH_2I(g))$ by means of the equation

$$\Delta H_f°(C_6H_5CH_2I(g)) = \Delta H°_{298} - \Delta H_f°(HI(g)) + \Delta H_f°(C_6H_5CH_3(g)) + \Delta H_f°(I_2(g))$$

Using the tabulated data,[2] this gives $\Delta H_f°(C_6H_5CH_2I(g))_{298} = 30.43 \pm 0.32$ kcal/mole. The error is a standard error and the same as that associated with $\Delta H°_{298}$ since other heats of formation are well known and easily measured, and the errors associated with them may be reasonably expected to be negligible.

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(9) F. T. Land and R. L. Strong, *J. Am. Chem. Soc.*, **87**, 2345 (1965).

(10) Calculation made from equation $C_p°(\text{R–I}) - C_p°(\text{R–H}) = C_p°(CH_3I) - C_p°(CH_3Cl) + C_p°(C_2H_5Cl) - C_p°(C_2H_6)$, using data at 298, 400, 500, 600, and 700°. Individual $C_p°$ values come from K. E. Howlett, *J. Chem. Soc.*, 1784 (1955), for C_2H_5Cl; E. Gelles and K. S. Pitzer, *J. Am. Chem. Soc.*, **75**, 5259 (1953), for CH_3I and CH_3Cl; and ref 2a for C_2H_6. CH_4 and CH_3I were not used for direct comparison since they have no hindered internal rotations.

(11) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958).

Table I. Equilibrium Data for the System[a] $C_6H_5CH_3 + I_2 \rightleftarrows C_6H_5CH_2I + HI$

Temp, °C	Time,[b] min	$[I_2]_0$	$[C_6H_5CH_3]_0$	$[HI]_0$	$[C_6H_5CH_2I]_{eq}$	10^4K_{eq}
207.6	100, 220	27.6	11.74	2.87	0.0112	0.996
207.6	85, 135	27.6	37.4	2.87	0.0286	0.807[c]
207.7	60, 194	5.96	101.7	2.09	0.0219	0.765[c]
207.7	...159	6.19	45.8	0.632	0.0381	0.906
207.5	135, 230	30.1	81.7	1.328	0.127	0.755
218.1	90, 130	3.52	47.9	0.488	0.0379	1.172
218.1	64, 81	3.52	85.8	0.488	0.0577	1.063[c]
218.0	60, 82	33.05	55.5	2.945	0.0548	0.899
240.5	30, 110	42.9	13.15	2.6	0.0395	1.774[d]
240.0	20, 80	1.776	297.0	0	0.0272	1.639[e]
239.8	11, 15	16.64	43.7	2.97	0.0391	1.623
239.8	10, 13	16.64	84.5	2.97	0.0662	1.440[c]
239.8	10, 14	16.64	102.7	2.97	0.0797	1.434[c]
239.8	18, 26	4.53	52.4	1.024	0.0361	1.628
239.8	24, 35	4.53	111.5	1.024	0.0702	1.545[c]
239.8	30, 40	31.8	11.3	1.924	0.0305	1.658
239.8	25, 42	31.8	49.0	1.924	0.1151	1.510[c]
270.0	4, 8	11.43	52.0	1.632	0.0812	2.365
270.0	3, 7.5	11.43	104.5	1.632	0.1273	1.895[f]
270.0	4, 9	29.6	30.5	3.15	0.0703	2.525
270.0	3, 6.5	29.6	70.8	3.15	0.1510	2.39[c]
269.9	4, 7, 12	2.66	50.8	0.936	0.0322	2.33
269.9	2, 5, 8	2.66	104.8	0.936	0.0572	2.09[c]
269.8	4, 9	26.17	29.5	2.95	0.0687	2.71[d]
300.3	1, 5	13.2	50.9	2.30	0.1137	4.12
300.3	1.5, 5	13.2	85.0	2.30	0.1744	3.91[c]
300.3	1.5, 5	30.4	29.9	3.33	0.1090	4.16
300.0	1.5, 5	2.57	50.2	1.064	0.0499	4.39
300.0	1.5, 5	2.57	100.9	1.064	0.0890	4.11[c]
330.7	Inst, 5	2.203	51.1	1.184	0.0603	6.87
330.7	Inst, 5	2.203	102.0	1.184	0.1108	6.74[c]
330.8	Inst, 5	26.4	15.0	9.32	0.0292	6.90
330.8	Inst, 5	26.4	43.1	9.32	0.0772	6.42[c]
330.5	Inst, 5	11.19	31.6	2.35	0.0938	6.55
330.5	Inst, 5	11.19	70.7	2.35	0.1935	6.34[c]
332.5	10, 15	2.10	320.6	0	0.506	5.44[e]
362.3	Inst	1.18	49.7	1.60	0.0415	12.01
362.3	Inst	1.18	102.3	1.60	0.0727	10.71
362.9	Inst	5.14	33.6	6.20	0.0351	12.79
362.4	Inst	29.4	10.6	11.0	0.0344	12.15
362.4	Inst	29.4	31.8	11.0	0.0815	9.74[c]
362.5	Inst	30.6	10.7	6.3	0.0532	10.45
392.6	Inst	1.992	50.2	5.26	0.0354	19.11
392.6	Inst	1.992	91.2	5.26	0.0591	17.86[c]
393.2	Inst	31.0	11.8	15.8	0.0416	17.97
392.9	Inst	8.47	30.3	9.70	0.0450	17.21
392.9	Inst	8.47	57.9	9.70	0.0766	15.47[c]

[a] All pressures listed in torr. [b] Times listed are time to reach equilibrium and time at which equilibrium absorbances were checked and found unaltered (Inst = instantaneous). [c] The runs were performed by pressurizing an established equilibrium with toluene. [d] The runs were performed by pressurizing an established equilibrium with HI. [e] In these runs the $[I_2]$ loss was recorded. It always corresponded to within 8% to $[C_6H_5CH_2I]_{eq}$. [f] This value was rejected since it was more than 2.5 standard deviations from the mean.

Table II. Literature Data for Entropy Calculation

Entropy at 298°K	Value	Ref
$S°(C\text{–}I(g))$	24.65	11
$S°(C\text{–}H(g))$	12.90	11
Symmetry = $R \ln 3$	2.18	
$S°(C_6H_5CH_2I(g)) - S°(C_6H_5CH_3(g))$	13.93	
$S°(HI(g))$	49.35	2
$S°(I_2(g))$	62.28	2
$\Delta S°_{298}$	+1.00	

Kinetic Measurements. Kinetic measurements were only possible over the limited temperature range 207–270°. Without premixing of the reactants, the initial rate measurements were necessarily crude. However, it was evident from the continuous absorbance record that mixing was fairly rapidly achieved, and only began to compete, as a rate-controlling step, with chemical reaction above 270°. Below 207° there was some evidence of heterogeneity, and an enhanced reaction in the region where equilibrium constants showed irreproducible rate behavior. The reaction vessel surface area-to-volume ratio was not varied during these experiments.

The rate measurements were interpreted in accordance with the now well-established mechanism[12] for reaction between I_2 and RH.

$$M + I_2 \rightleftharpoons 2I\cdot + M \quad K_{I_2} \tag{i}$$

$$I\cdot + C_6H_5CH_3 \underset{k_3}{\overset{k_4}{\rightleftharpoons}} C_6H_5CH_2\cdot + HI \tag{ii}$$

$$C_6H_5CH_2\cdot + I_2 \underset{k_1}{\overset{k_2}{\rightleftharpoons}} C_6H_5CH_2I + I\cdot \tag{iii}$$

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(12) (a) S. W. Benson and H. E. O'Neal, *J. Chem. Phys.*, **34**, 514 (1961); (b) S. W. Benson and P. S. Nangia, *J. Am. Chem. Soc.*, **86**, 2773 (1964); (c) S. W. Benson and H. Teranishi, *ibid.*, **85**, 2890 (1963).

Table III. Kinetic Data for the Reaction $I + C_6H_5CH_3 \xrightarrow{k_4} C_6H_5CH_2 + HI$

Temp, °C	$10^5\left\{\frac{\partial[C_6H_5CH_2I]}{\partial t}\right\}_{t_0}$ torr/sec	$[C_6H_5CH_3]_0$, torr	$[I_2]_0$, torr	$10^4[I]$,[a] torr	10^3k_4, torr^{-1} sec^{-1}
182[b]	0.805	45.0	5.10	0.5888	3.04
	2.01	34.1	5.06	0.585	10.08
	1.054	5.17	22.3	1.229	16.62
	1.05	98.3	5.38	0.596	1.79
207.8	3.50	47.3	5.35	1.731	4.27
	1.125	14.0	23.5	3.64	2.21
	0.805	11.74	27.6	3.94	1.742
	1.005	23.75	5.96	1.831	2.31
	2.23	45.8	6.19	1.869	2.49
	1.275	8.58	25.6	3.80	3.91
	5.63	81.7	30.1	4.11	1.935
				Mean value	2.69 ± 0.99
218.0	4.32	47.9	3.52	2.06	4.38
	6.98	55.5	33.05	6.31	1.99
				Mean value	3.18 ± 1.20
240.0	24.6	71.8	4.31	5.22	6.56
	27.2	121.2	3.77	4.87	4.60
	11.6	10.42	32.2	14.24	7.80
	13.4	13.5	42.9	16.41	6.05
	24.6	31.4	30.0	13.74	5.70
	75.0	297.0	1.776	3.34	7.56
	32.5	103.6	6.56	6.43	4.88
	95.8	93.7	28.7	13.44	7.60
	23.4	79.7	5.05	5.65	5.20
	35.3	43.7	16.60	10.23	7.89
	14.9	52.4	4.53	5.35	5.31
	11.2	11.3	31.8	14.14	7.00
				Mean value	6.35 ± 1.21
270.0	149.1	78.8	4.41	14.19	13.33
	101.4	52.0	11.43	22.8	8.55
	90.4	30.5	29.6	36.7	8.08
	88.5	50.8	2.66	11.00	15.55
	153.0	29.5	26.17	34.5	15.04
				Mean value	12.11 ± 3.56

[a] [I] was calculated from equilibrium relationship $K_{I_2} = [I]^2/[I_2]$. K_{I_2} was calculated from the JANAF tables.[2b] [b] Values of k_4 at this temperature are shown in Figure 3 but not included in estimate of line of best fit.

Previous studies of these systems indicate that, in the initial stages, step 4 is the rate-controlling step (even in the presence of HI) and therefore that

$$\left(\frac{d[C_6H_5CH_2I]}{dt}\right)_{t_0} = \left(\frac{d[HI]}{dt}\right)_{t_0} = k_4[I][C_6H_5CH_3] = k_4K_{I_2}{}^{1/2}[I_2]^{1/2}[C_6H_5CH_3]$$

Thus the initial rates of benzyl iodide can be readily converted into values for k_4. These values were calculated and together with the other relevant kinetic data are listed in Table III. In spite of the fairly wide scatter of values of k_4 at any given temperature, the deviation of the means is not exceptionally large and the range of initial values for $[C_6H_5CH_3]/[I_2]$ has been varied by more than a factor of 25 at all temperatures.

An Arrhenius plot of these data was made and is shown in Figure 3 with flags on the points to indicate error limits. The line of best fit through these points has been drawn, and the slope and intercept have been measured, the error being estimated to accommodate half the spread of values of k_4 at the extremes of the temperature range.

The Arrhenius parameters derived from this plot when converted to concentration units give

$$\log k_4\,(\text{l./mole sec}) = 8.43 \pm 1.22 - \frac{14.4 \pm 2.9}{\theta}$$

If it is assumed that the back reaction has an activation energy $E_3 = 1.5 \pm 1.0$ kcal/mole,[13] then $\Delta H°_{4,3}(513°K) = E_4 - E_3 = 12.9 \pm 3.1$ kcal/mole. It is unlikely that $\overline{\Delta C}_{p4,3}$ is very far from zero which means that $\Delta H°_{4,3}(298°K) = 12.9 \pm 3.1$ kcal/mole. This result makes possible the calculation of the benzyl radical heat of formation from the equation

$$\Delta H_f°(C_6H_5CH_2\cdot(g)) = \Delta H°_{4,3} - \Delta H_f°(HI(g)) + \Delta H_f°(C_6H_5CH_3(g)) + \Delta H_f°(I(g))$$

Substituting the tabulated data,[2] the value obtained is $\Delta H_f°(C_6H_5CH_2\cdot(g))_{298} = 44.1 \pm 3.1$ kcal/mole. Moreover, the following bond strengths may be calculated

$$DH°(C_6H_5CH_2\text{–}H)_{298} = \Delta H_f°(C_6H_5CH_2\cdot(g))_{298} + \Delta H_f°(H(g))_{298} - \Delta H_f°(C_6H_5CH_3(g))_{298}$$

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(13) This is found to be the best value for reactions of type 3 on the basis of several measurements of the competitive reaction of I_2 and HI with different radicals[12a] and an assumption that radicals react with I_2 with zero activation energy.

and

$$DH^\circ(C_6H_5CH_2\text{-}I)_{298} = \Delta H_f^\circ(C_6H_5CH_2\cdot(g))_{298} + \Delta H_f^\circ(I(g))_{298} - \Delta H_f^\circ(C_6H_5CH_2I(g))_{298}$$

Inserting the tabulated data,[2] and the value for $\Delta H_f^\circ(C_6H_5CH_2I(g))_{298}$ derived from this work, gives $DH^\circ(C_6H_5CH_2\text{-}H)_{298}$ = 84.2 ± 3.1 kcal/mole and $DH^\circ(C_6H_5CH_2\text{-}I)_{298}$ = 39.2 ± 3.1 kcal/mole.

Discussion

The original measurements of $\Delta H_f^\circ(C_6H_5CH_2I(l))_{298}$ of Skinner and Gellner[14] have been corrected for more recent calorimetric data and better heats of vaporization by Benson and Buss,[4] who suggest a value of $\Delta H_f^\circ(C_6H_5CH_2I(g))_{298}$ = 29.2 ± 3 kcal/mole. Our more precise value is in good agreement with this. More recently[15] a value of +23.9 ± 0.4 kcal/mole has been obtained by a calorimetric method involving reduction of benzyl iodide in ethereal solution with lithium aluminum hydride. The discrepancy between this and our value is rather large and we are, at present, unable to offer any explanation for this.

The controversy over the heat of formation of the benzyl radical and the bond strength in toluene, $DH^\circ(C_6H_5CH_2\text{-}H)_{298}$, has been somewhat clarified by Trotman-Dickenson and co-workers[6] who report two new measurements of 84.6 ± 1.5 kcal/mole for the bond strength, using an aniline carrier technique. This method appears not to be subject to the uncertainties of the toluene carrier technique.[16] However, recently Price[17] has used the latter technique under optimum conditions to obtain an activation energy of 85 kcal/mole for homogeneous toluene pyrolysis, which he attributes to $DH^\circ(C_6H_5CH_2\text{-}H)_{298}$. He also discusses the reasons why this is to be preferred to Szwarc's earlier value of 77.5 kcal/mole.[18] Trotman-Dickenson, *et al.*,[6] have also presented arguments that two further pieces of work[19,20] should lead to separate values of 85.0 and 86.5 kcal/mole for $DH^\circ(C_6H_5CH_2\text{-}H)_{298}$. The weight of evidence would seem to favor a value of 85.0 ± 1.0 kcal/mole with which our new figure is in excellent agreement. Although it is certainly possible to refine the somewhat crude kinetic measurements of this work, we feel that the above agreement makes this superfluous.

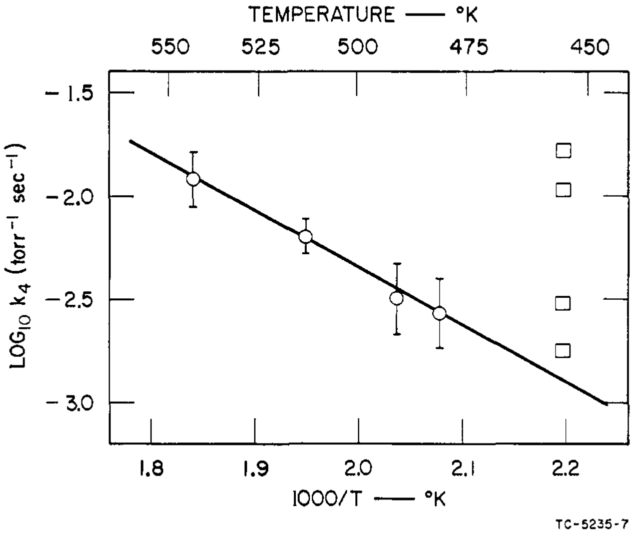

Figure 3. Arrhenius plot of the rate constant for iodine atom abstraction from toluene: line drawn represents best fit by eye; data not sufficiently precise to warrant least-mean-squares fit; points marked □ not included in estimate of line.

The bond strength $DH^\circ(C_6H_5CH_2\text{-}I)_{298}$ was first reported by Szwarc[21] who obtained a value of 39.0 kcal/mole to which a correction was subsequently applied by Benson and Buss[4] giving a figure of 40.3 kcal/mole. More recently Horrex, *et al.*,[22] proposed 40.6 kcal/mole for the bond strength. Thus, our work is also in excellent agreement with these results and we suggest that $DH^\circ_{298}(C_6H_5CH_2\text{-}I)$ = 40.0 ± 1.0 kcal/mole. To be consistent with these bond energies, $\Delta H_f^\circ(C_6H_5CH_2(g))$ = 44.9 ± 1.0 kcal/mole.

The usual working definition of resonance energy is the energy difference between a C–H bond conjugated with a double bond, or aromatic ring system, and a similar bond in a saturated paraffin. For the latter, a value of 97.5 kcal/mole may be regarded as representative for primary C–H bonds (*e.g.*, in ethane[23] or propane[24]; methane should not be used for comparison since its bond strength[3] is not typical). Thus the benzyl resonance energy turns out to be 12.5 ± 1.0 kcal/mole, very close in value to the allyl resonance energy of 12.6 ± 1.0 kcal/mole.[25]

Individual Rate Constants and Arrhenius Parameters. On the basis of the bond energies proposed in the previous section and a reasonable estimate of the entropy of the benzyl radical, it is now possible to evaluate the Arrhenius parameters for the individual reactions of the mechanism proposed for the present system. These are summarized in Table IV. It has been assumed in deriving these data that E_2 = 0, E_3 = 1.5 kcal/mole, and that log A_2/A_3 = 0.5 ± 0.5, by analogy with similar systems.[13]

Table IV. Summary of Arrhenius Parameters at 500°K

Reaction	Log *A*, l/mole sec	*E*, kcal/mole
1	8.75 ± 0.5	3.5 ± 1
2	7.75 ± 0.5	0 ± 1
3	7.25 ± 0.5	1.5 ± 1
4	8.75 ± 0.5	15.2 ± 1

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(14) O. H. Gellner and H. A. Skinner, *J. Chem. Soc.*, 1145 (1949).

(15) S. J. Ashcroft, A. S. Carson, and J. B. Pedley, *Trans. Faraday Soc.*, **59**, 2713 (1963).

(16) M. Szwarc, *J. Chem. Phys.*, **17**, 431 (1949).

(17) S. J. Price, *Can. J. Chem.*, 40, 1310 (1962).

(18) M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).

(19) H. R. Anderson, H. A. Scheraga, and E. R. Van Artsdalen, *ibid.*, 21, 1258 (1953).

(20) (a) W. K. Busfield and K. J. Ivin, *Trans. Faraday Soc.*, **57**, 1044 (1961); (b) W. K. Busfield, K. J. Ivin, H. Mackle, and P. A. G. O'Hare, *ibid.*, 57, 1064 (1961).

(21) M. Szwarc, Thesis, Manchester University, 1947.

(22) R. K. Boyd, G. W. Downs, J. S. Gow, and C. Horrex, *J. Phys. Chem.*, **67**, 719 (1963).

(23) D. B. Hartley and S. W. Benson, *J. Chem. Phys.*, **39**, 132 (1963).

(24) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 123 (1961).

(25) (a) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964); (b) A. S. Rodgers, D. M. Golden, and S. W. Benson, to be published.

The entropy estimate for the benzyl radical has been made as follows.

$S°_{298}(C_6H_5CH_2\cdot) = S°_{298}(C_6H_5CH_3) - 0.8$ (loss of hydrogen deformation mode) $+ R \ln 3$ (symmetry changes) $+ R \ln 2$ (electronic degeneracy) $- 3.0$ (loss of internal rotation in resonance stiffened radical) $= S°_{298}(C_6H_5CH_3) - 0.3$

It was assumed that this difference did not alter with temperature. This was considered uncertain to ±1 gibbs/mole. In conjunction with the listed entropies,[2] this gave $\Delta S°_{1,2}(500°K) = +4.51 \pm 1$ and $\Delta S°_{3,4}(500°K) = -6.93 \pm 1$ gibb/mole. Thus the ratios A_1/A_2 and A_3/A_4 could then be evaluated and the individual A factors separated by substitution of A_4 and A_2/A_3. The Arrhenius parameters for k_4 are a refinement of our measured value obtained by assuming the global rate constant is correct and adjusting the activation energy (within its standard error) to give the correct toluene bond strength.

A comparison of this system with similar systems[12a] involving $I_2 + RH$ reveals that the A factors here are all about $10^{2.5}$ lower than those where R is not a resonance-stabilized radical. This indicates that the transition states are extremely tight for reactions $1 \rightleftarrows 2$ and $3 \rightleftarrows 4$. A similar stiffening was found for the case where $R \equiv$ methylallyl[25a] or allyl.[25b]

The Reaction of Hydrogen Atoms with Some Conjugated Ring Systems at 77°K[1]

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Abstract: Binary mixtures of naphthalene with methanol and ethanol have been irradiated with X-rays at 77°K and studied by esr methods. Previous work has determined that, upon irradiation, the hydroxyl hydrogen is liberated and subsequently adds on to the conjugated ring system. With naphthalene, the hydrogen atom adds on in the α position. Molecular orbital calculations of the cyclohexadienyl radical and the corresponding naphthalene radical show good agreement with the data obtained.

This paper presents further studies on the irradiation of binary mixtures of conjugated ring systems and simple alcohols. Earlier studies[2] utilizing benzene in methanol and ethanol reveal that, upon irradiation at 77°K, a hydroxyl hydrogen atom is released. This hydrogen atom then can form H_2 by combining with another hydrogen atom and by abstraction of a hydrogen from the alcohol matrix or can add on to the benzene ring to form the cyclohexadienyl radical. At temperatures slightly warmer than that of liquid nitrogen, all other radical species decay, and the esr spectrum of the cyclohexadienyl radical is obtained with measured splitting constants that agree with other work.[3,4] In this study, naphthalene and various methyl-substituted benzenes such as toluene, xylene, and mesitylene were studied in mole percentages ranging from 1 to 5 mole %.

Experimental Section

Reagent grade chemicals without further purification were used throughout this study. The isotopically substituted naphthalene-d_8 and methanol-d were obtained from Volk Radiochemical Company and have a minimum isotopic purity of 98 atom %. The irradiation procedure and detection equipment have been discussed elsewhere.[2] The solubility of naphthalene in both methanol and ethanol is much less than 5 mole %. The procedure used was to make a concentrated solution of naphthalene in the alcohol, and then dilute with more alcohol until the solution formed glassy spheres when droplets were dropped into liquid nitrogen. The dilution was a factor of 2 to 4 times that of concentrated solution. A small amount of ethyl ether had to be added to the mesitylene-methanol solution so that a glass could be formed. The same amount of ether was added to the xylenes also without altering the results.

Results and Discussion

A. Naphthalene. Figure 1 shows the spectrum obtained of the naphthalene radical in methanol after warming up and permitting the methanol triplet to decay. The spectrum consists of a 37-gauss 1:2:1 triplet due to two hydrogen atoms at position 1, the site attached by the free hydrogen atom. These lines are then split into 12.8-gauss 1:2:1 triplets due to the nearly equivalent hydrogens at positions 2 and 4. Position 3 should give a doublet splitting of 3.1 gauss, but it is not resolvable. Positions 5 through 8 have very low spin density as will be shown by the calculations.

Figure 2 shows the results of the isotopic runs. In Figure 2A, naphthalene was irradiated in a matrix of MeOD. The deuterium from the matrix adds to position 1, and the hydrogen doublet from position 1 is clearly visible. The splittings due to the hydrogens at sites 2 and 4 are visible, but one has some trouble (as was the case with C_6H_6 in MeOD) finding the deuterium triplet. Figure 2B shows $C_{10}D_8$ in MeOD and the 1:2:3:2:1 quintuplet from the two sp^3 deuteriums is readily visible. Figure 2C shows $C_{10}H_8$

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(1) This investigation was supported in part by Research Grant GM 5144 from the Division of General Medical Sciences, Public Health Service, National Institutes of Health.

(2) J. A. Leone and W. S. Koski, *J. Am. Chem. Soc.*, **88**, 224 (1966).

(3) S. Ohnishi, T. Tanei, and I. Nitta, *J. Chem. Phys.*, **37**, 2402 (1962).

(4) H. Fischer, *Kolloid-Z.*, **180**, 64 (1964).