that the aqueous product solutions be brought to pH 12.0 before extraction with ether in order to allow quantitative extraction of the unreacted quinuclidine; for each sample the pH was checked before each of the four successive extractions and aqueous NaOH added as required.

Acknowledgment. This material is based on work supported by the National Science Foundation under Grant CHE-8304874.

Registry No. 4-MePy, 108-89-4; Py, 110-86-1; 3-AcPy, 350-03-8; Q, 100-76-5; ^{15}N, 14390-96-6; *N,N*-dimethyl-4-methylaniline, 99-97-8.

Thermal Decomposition of Phenyl Iodide and *o*-Iodotoluene

D. Robaugh[†] **and W. Tsang***

Chemical Kinetics Division, National Bureau of Standards, Gaithersburg, Maryland 20899
(Received: February 13, 1986)

Phenyl iodide and *o*-iodotoluene have been decomposed in comparative-rate single-pulse shock-tube experiments using cyclopentane as a source of abstractable H atoms. The conditions for quantitative conversion of phenyl radical to benzene and *o*-methylphenyl radical to toluene are determined. On the basis of the reverse Diels–Alder reaction of 1,2-dimethylcyclohexene (1,2-DMC) as the internal standard, the rate expressions for phenyl iodide and *o*-iodotoluene decomposition have been found to be $k(\text{phenyl–I} \rightarrow \text{phenyl} + \text{I}) = 8.6 \times 10^{14} \exp(-32\,821/T)\ \text{s}^{-1}$ and $k(o\text{-iodotoluene–I} \rightarrow o\text{-methylphenyl} + \text{I}) = 1.4 \times 10^{15} \exp(-33\,346/T)\ \text{s}^{-1}$ at 1100 K and between 2 and 6 atm. Ortho methyl substitution has negligible effect on the rate of C–I bond cleavage under these conditions. The present results lead to a heat of formation for phenyl radical of 340.5 ± 11 kJ/mol or a bond dissociation energy for the C–H bond in benzene of 475 ± 11 kJ. At 1100 K, the rate constant for the combination of phenyl radical and iodine atom is near 1×10^{10} L/(mol·s), while the rate constant for phenyl attack on cyclopentane is $\leq 3 \times 10^{8}$ L/(mol·s). In addition, we call attention to the rate expression for 1,2-dimethylcyclohexene (1,2-DMC) decomposition, $k(1,2\text{-DMC}) = 3.2 \times 10^{15} \exp(-35\,228/T)\ \text{s}^{-1}$, which we determined from our comparative rate studies with cyclohexene and 1-methylcyclohexene as internal standards. It is suggested that the larger rate parameters may mark the onset of a diradical contribution to 1,2-dimethylcyclohexene decomposition.

Introduction

This paper is concerned with the unimolecular decomposition of phenyl iodide and *o*-iodotoluene. Experiments are carried out in a heated single-pulse shock tube using cyclopentane[1] as a radical scavenger and in the presence of an internal standard. The extent of reaction is determined by measuring the amount of benzene or toluene formed in the system via the reactions

$$\text{phenyl}/o\text{-methylphenyl} + \text{cyclopentane} \rightarrow \text{benzene/toluene} + \text{cyclopentyl}$$

Kominar, Krech, and Price[2] have previously studied the decomposition of phenyl iodide in toluene carrier experiments. The main reaction is the breaking of the C–I bond. On the basis of iodobenzene disappearance they derived the rate expression

$$k(\text{phenyl–I} \rightarrow \text{phenyl} + \text{I}) = 2.6 \times 10^{14} \exp(-31\,313/T)\ \text{s}^{-1}$$

However, in order to obtain results that are more compatible with generally accepted bond energies and radical combination rates, they scaled their values and recommended the rate expression

$$k(\text{phenyl–I} \rightarrow \text{phenyl} + \text{I}) = 1 \times 10^{15} \exp(-32\,445/T)\ \text{s}^{-1}$$

Comparative rate single-pulse shock tube experiments[3] can yield highly precise rate expressions. Checks with the literature have also indicated high accuracy.[3] Uncertainties in absolute magnitude are a factor of 1.5 for A factors and 4 kJ/mol in the activation energies. Past work has demonstrated that the A factors are relatively invariant for similar types of reactions.[3] Thus the present work should lead to an estimation of the A factors for the breaking of other aromatic halide bonds. We should also be able to determine the heat of formation of the phenyl radical. McMillen and Golden[4] have recommended a value of 328.4 ± 8 kJ/mol. Recently, we have shown that the generally accepted values for the heat of formation of simple alkyl radicals are inconsistent with the available kinetic data on alkane decomposition and formation (from alkyl radicals) and alkyl radical decomposition and their reverse addition process by 10–20 kJ/mol.[5] These are based on a third-law analysis of the data.[5] It is preferred over the second-law treatment to be used here since the methodology is subject to a number of assumptions. Nevertheless, it should be noted that the difference in the heat of formation of the alkyl radicals was first noted from similar comparative-rate single-pulse shock-tube experiments.[6] A new determination of the heat of formation of phenyl radical should be very useful in view of its importance in high-temperature pyrolysis systems. Furthermore, with the proper thermochemistry it will be much easier to interpret the available kinetic data on phenyl radical reactions. There has not been any prior study on the decomposition of *o*-iodotoluene. The interest here is in the possibility of new channels for decomposition and the effect of the methyl group on the rate constant for C–I bond cleavage.

Experimental Section

Our studies are carried out in a heated single-pulse shock tube that we have recently assembled. Except for the fact that it is made from square 1.25-in. aluminum tubing, it is similar to that used in our earlier experiments.[3] The low-pressure section was heated by heating tape wound about an outer 6-in. aluminum tube. Temperatures were maintained at 100 ± 0.5 °C. The driver section and the entire gas handling system were also heated and maintained at an elevated temperature over the course of all the experiments. Heating the entire system enabled us to introduce

---

[†] Present address: Midwest Research Institute, 425 Volker Boulevard, Kansas City, MO 64110.

(1) Tsang, W. *J. Phys. Chem.* **1984**, *88*, 2812.

(2) Kominar, R. J.; Krech, M. J.; Price, S. J. W. *Can. J. Chem.* **1976**, *54*, 2911.

(3) Tsang, W. In *Shock Waves in Chemistry*; Lifshitz, A., Ed.; Marcel Dekker: New York, 1981; p 59.

(4) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(5) Tsang, W. *J. Am. Chem. Soc.* **1985**, *107*, 2072.

(6) Tsang, W. *Int. J. Che. Kinet.* **1978**, *10*, 821.

and extract from the shock tube compounds of low volatility.

Analysis of reactant and product gases is by gas chromatography with flame ionization detection. The columns used are 6-ft bentone at 100 °C and 12-ft silicone oil at 88 °C. They are connected in such a way that all compounds up to the iodoaromatics are eluted in a reasonable time. The iodo compounds and the cyclohexenes are from SCM.[7] Cyclopentane is from Wiley Organics and argon is of Ultrapure Grade and is from Matheson. Gas chromatography failed to reveal the presence of any impurity in the test gas. Thus, except for vigorous degassing of the organic samples, no attempt was made at further purification.

The internal standard used for these studies is the reverse Diels–Alder decomposition of 1,2-dimethylcyclohexene (1,2-DMC) to form ethylene and 2,3-dimethylbutadiene. This reaction was selected because with the chromatographic columns used in the present experiments, the 2,3-dimethylbutadiene eluted in a convenient time. Since rate expressions for this reaction do not exist, the first studies involved comparative rate experiments on the decomposition of 1,2-dimethylcyclohexene, using as internal standards the decomposition of cyclohexene (CH) and 1-methylcyclohexene (1-MCH).[3]

Crucial to the success of these experiments is the effectiveness of cyclopentane as a radical scavenger. This involves not only its reactions with reactive species but also the stability of the cyclopentyl radical. The latter decomposes via the reactions

$$\text{cyclopentyl} \rightarrow \text{cyclopentene} + \text{H}$$

$$\text{cyclopentyl} \rightarrow \text{allyl} + C_2H_4$$

$$\text{H} + \text{cyclopentane} \rightarrow \text{cyclopentyl} + H_2$$

The allyl radical is fairly stable within the time scale of these experiments (500 μs). Furthermore, as long as the cyclopentane remains in large excess, the phenyl iodide is protected from radical-induced decomposition, unless the rates of radical attack on cyclopentane are much slower than on phenyl iodide. The effectiveness of cyclopentane as an inhibitor against such processes has been demonstrated in an earlier study.[1] There we showed that in the decomposition of BrC_2F_4Br in cyclopentane at temperatures up to 1100 K exactly two ethylene molecules are formed for every perfluoroethylene molecule detected. In the present case we are using the cyclopentane as a source of hydrogen atoms for phenyl and *o*-methylphenyl radicals. The conditions under which quantitative conversions to benzene or toluene occur can then be used in subsequent studies to account for the number of phenyl type radicals in a reactive system.

Of key importance to the quantitative validity of these experiments is the necessity for the complete conversion of all the phenyl radicals to benzene. Unfortunately, data on the reactivity of phenyl radicals are scarce. In order to attest to complete conversion, experiments have been carried out with a whole range of cyclopentane concentrations. The ratio of cyclopentane to the aromatic iodide concentrations varied between 100 and 300. The cyclopentane concentration varied from 0.1 to 5%. The reaction pressure ranged from 2 to 6 atm. The large excess of cyclopentane serves as a radical trap and makes impossible the radical-induced decomposition of the iodoaromatic compounds. It is expected that as the cyclopentane concentration is reduced there will come a point below which phenyl radical conversion to benzene will be incomplete. This will be demonstrated by failure in material balance and systematic deviations in the comparative rate plots. It will permit a limit to be set on the minimum level of cyclopentane for our purposes.

In earlier studies with cyclopentane as the scavenger, the yields of ethylene also served as a marker for the number of radicals released into the system. This did not prove to be feasible in the present instance, because the rate constant for iodine attack on cyclopentane is sufficiently slow so that there is considerable uncertainty as to whether all the iodine radicals can be trapped in this manner. Furthermore, the aromatic iodides used in these studies are considerably more stable than the allyl bromide and dibromoperfluoroethane used in our earlier studies. Thus the 1100 K limit beyond which the decomposition products from cyclopentane pyrolysis will begin to have an interfering effect on the light hydrocarbon yields must be exceeded. Our experiments are carried out in the 1050–1200 K range. At the higher temperature end of this range, our previous[8] studies have demonstrated that the direct products from cyclopentane decomposition (present in 100- to 300-fold excess over the aromatic iodide) are close to or may even exceed the light hydrocarbon yields originating from the induced decomposition of the cyclopentane (due to aromatic iodide decomposition). However, cyclopentane decomposition under the present conditions does not form benzene. Benzene formed in these experiments must have originated from phenyl radicals. Demonstration of proper material balance also implies the possibility of using the benzene yield as a marker of reaction extent. Accordingly, we focus attention in these experiments on the quantity of benzene or toluene formed, the amount of phenyl iodide or *o*-methylphenyl iodide lost, and the yields of 2,3-dimethylbutadiene from the decomposition of the standard.

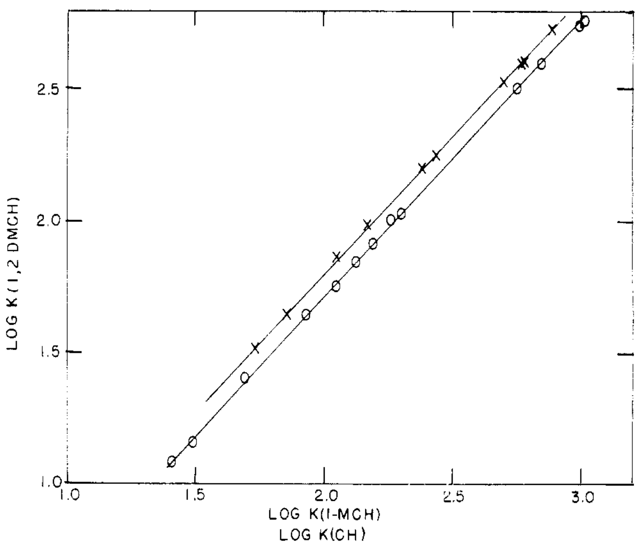

Figure 1. Comparative-rate single-pulse shock-tube results on the decomposition of 207 ppm 1-methylcyclohexene (1-MCH) and 207 ppm 1,2-dimethylcyclohexene (1,2-DMCH) in 5% toluene and argon (×) and 290 ppm cyclohexene (CH) and 204 ppm 1,2-dimethylcyclohexene (1,2-DMCH) in 5% cyclopentane and argon (○). Reaction pressure is approximately 3 atm. Temperature is 1060–1200 K. Heating time is 500 μs.

Results

The initial studies involve the determination of the rate parameters for the decomposition of the internal standard, 1,2-dimethylcyclohexene (1,2-DMC). The results of comparative rate experiments with cyclohexene (CH) and 1-methylcyclohexene (1-MCH) decomposition as calibrants and with the butadienes as the markers for the extent of reaction are plotted in Figure 1. The least-squares relations are as follows:

$$\log k(\text{1,2-DMC}) = (1.052 \pm 0.003) \log k(\text{CH}) - (0.392 \pm 0.007)$$

$$\log k(\text{1,2-DMC}) = (1.049 \pm 0.005) \log k(\text{1-MCH}) - (0.305 \pm 0.01)$$

Using $k(\text{CH}) = 1.4 \times 10^{15} \exp(-33\,535/T)$ and $k(\text{1-MCH}) = 1.1 \times 10^{15} \exp(-33\,535/T)\ \text{s}^{-1}$,[3] we arrive at $k(\text{1,2-DMC}) = 3.5 \times 10^{15} \exp(-35\,278/T)\ \text{s}^{-1}$ with the cyclohexene standard and

---

[7] Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment is the best available for the purpose.

[8] Tsang, W. *Int. J. Chem. Kinet.* **1978**, *10*, 599.

TABLE I: Mass Balances at Higher Extents of Decomposition for Iodobenzene (IBz) and *o*-Iodotoluene (ITol) at 1175 K, 3 atm, and 500 μs Heating Time

	$RH/(RI)_i$	$(RI)_f/(RI)_i$	$(RH + (RI)_f)/(RI)_i$
	Iodobenzene		
5.1% cyclopentane 181 ppm IBz	0.263	0.730	0.993
1% cyclopentane 35 ppm IBz	0.262	0.738	1.00
0.2% cyclopentane 6.9 ppm IBz	0.222	0.761	0.983
0.1% cyclopentane 3.4 ppm IBz	0.183	0.701	0.884
	o-Iodotoluene		
5% cyclopentane 216 ppm ITol	0.267	0.720	0.987

$k(\text{1,2-DMC}) = 3.0 \times 10^{15} \exp(-35178/T)\ \text{s}^{-1}$ with the 1-methylcyclohexene standard. The expression that will be used in the subsequent analysis

$$k(\text{1,2-DMC} \rightarrow C_2H_4 + \text{2,3-DMB}) = 3.2 \times 10^{15} \exp(-35228/T)\ \text{s}^{-1}$$

is the average of the results of the two sets of experiments. It is interesting that there is a distinct difference in the rate expression for 1,2-dimethylcyclohexene decomposition as compared to the other two cyclohexenes. The results from the two independent set of experiments appear to confirm the unexpected result. Due to the molecular nature of these experiments the extra uncertainty introduced by the use of a "secondary" standard should be small. It is estimated that this will not exceed 1 kJ in the activation energy and a factor of 1.15 in the *A* factor.

The products from the decomposition of the aromatic iodides in the presence of large excesses of cyclopentane are ethylene, propylene, allene, 1-pentene, and benzene (or toluene in the case of *o*-iodotoluene decomposition). Ethylene is the most prominent reaction product. The aromatic compounds are also present in large quantities. As expected, a significant amount of the ethylene and propylene comes from the thermal unimolecular decomposition of cyclopentane itself (through 1-pentene).[8] The results summarized in Table I demonstrate the nature of the mass balances that can be obtained. For phenyl iodide, it can be seen that only at the lowest cyclopentane concentration is there a significant mass defect. The relationship between fractional conversion to benzene (F), rate constant for abstraction (k), and scavenger concentration (C) can be expressed to a very good approximation as

$$F = 1 - (1 - \exp(kCt))/(kCt)$$

where t is the residence time and is of the order of 500 μs. The data in Table I show that at a cyclopentane level of 0.1% we recover approximately 60% of the missing phenyl iodide as benzene. This means that $kC = 6 \times 10^3\ \text{s}^{-1}$. Most of the experiments have been carried out with cyclopentane concentrations of a factor of 50 higher. Here kC is equal to $3 \times 10^5\ \text{s}^{-1}$ and substitution into the above relation suggest conversions of greater than 99%. Indeed, even with 1% cyclopentane conversion exceeds 95%, as shown by our data in Table I. An important problem in single-pulse shock-tube experiments is the invariance of the heating time. Thus near the low-temperature limit (~1050 K) and correspondingly low conversions it is difficult to draw conclusions about mass balance by simply comparing product appearance and reactant disappearance. It is however possible to make some inferences on the basis of the comparative rate plots, where we compare the rate constant for unimolecular decomposition of our test molecule against the internal standard.

Figure 2 represents the results of studies on phenyl iodide. It consists of experiments with two different ratios of 1,2-dimethylcyclohexene and iodobenzene in very large excesses of cyclopentane. The experiments that contain the highest cyclopentane to iodobenzene ratio show a systematic deviation of 10% in the relative rate plots. This is about twice the standard deviation and is thus statistically significant. We are not certain of the cause of this discrepancy. It should have a minimal effect on our final results, since as can be seen in Figure 2 the comparative rate plots parallel each other and thus the changes in the rate expressions are insignificant within the context of these experiments. At a fixed iodobenzene to 1,2-dimethylcyclohexene to cyclopentane ratio no effect on the comparative rate plot could be observed when cyclopentane concentration is lowered to 1%. However, below this level deviations become increasingly large. This is in accord with our earlier discussion.

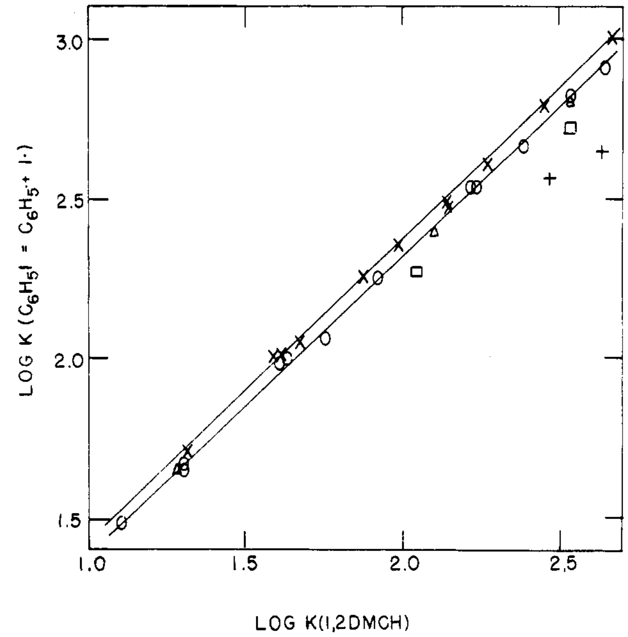

Figure 2. Comparative-rate single-pulse shock-tube results on the decomposition of iodobenzene ($C_6H_5I \rightarrow C_6H_5 + I$) with 1,2-dimethylcyclohexene decomposition as the internal standard and cyclopentane as the scavenger in argon at 2–6 atm pressure, temperature of 1000–1200 K and a heating time of 500 μs: (○) 181 ppm iodobenzene, 222 ppm 1,2-DMC, 51 000 ppm cyclopentane; (×) 110 ppm iodobenzene, 358 ppm 1,2-DMC, 49 000 ppm cyclopentane; (△) 35 ppm iodobenzene, 45 ppm 1,2-DMC, 10 000 ppm cyclopentane; (□) 7 ppm iodobenzene, 9.0 ppm 1,2-DMC, 2000 ppm cyclopentane; (+) 3.4 ppm iodobenzene, 4.3 ppm 1,2-DMC, 1000 ppm cyclopentane.

On this basis we conclude that the rate constant we calculate on the basis of the benzene and toluene yield faithfully reflects the rate of bond cleavage in phenyl iodide and *o*-iodotoluene, respectively. The least-squares relation from the comparative rate experiments with 36–180 ppm iodobenzene, 46–230 ppm 1,2-dimethylcyclohexene, and 1–5% cyclopentane in argon leads to

$$\log k(C_6H_5I \rightarrow C_6H_5 + I) = (0.930 \pm 0.006) \log k(\text{1,2-DMC}) + (0.456 \pm 0.012)$$

For studies with 110 ppm iodobenzene and 358 ppm 1,2-dimethylcyclohexene in 5% cyclopentane and argon we obtained

$$\log k(C_6H_5I \rightarrow C_6H_5 + I) = (0.934 \pm 0.007) \log k(\text{1,2-DMC}) + (0.504 \pm 0.015)$$

Thus except for the 10% deviation mentioned earlier, the relations are identical. Substitution into these relations of the rate expression for 1,2-dimethylcyclohexene decomposition derived earlier leads to the following average rate expression at 1100 K:

$$k(C_6H_5I \rightarrow C_6H_5 + I) = 8.6 \times 10^{14} \exp(-32821/T)\ \text{s}^{-1}$$

It should be noted that in our comparative rate experiments the pressure was varied by a factor of 3. Failure to observe any significant pressure dependence is indicative of our being at or very close to the high-pressure limit. From earlier studies[1] across such a pressure range we have established that a pressure dependence of the order of $p^{0.05}$ could be observed. There is no question that 1,2-dimethylcyclohexene decomposition is at the high-pressure limit.[1]

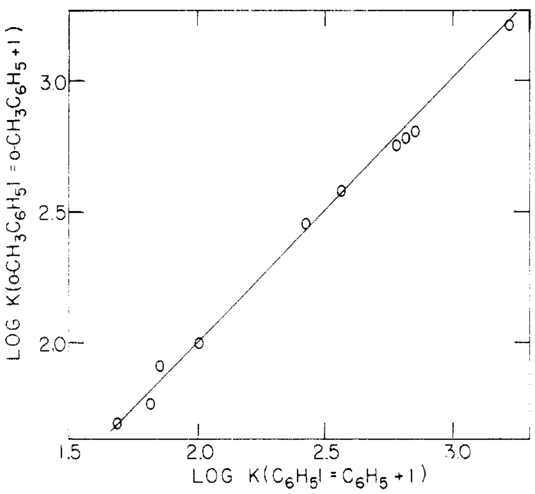

Figure 3. Comparative-rate single-pulse shock-tube results on the decomposition of iodobenzene (229 ppm) and *o*-iodotoluene (216 ppm) with 5% cyclopentane as the scavenger in argon at 3 atm. Temperature of 1000–1220 K, and a heating time of 500 μs.

Comparative rate plots of the decomposition of *o*-iodotoluene using phenyl iodide decomposition as the internal standard can be found in Figure 3. In these studies we use the benzene and toluene yields as markers for reaction extent. The rate relationship is

$$\log k(o\text{-}CH_3C_6H_4I \rightarrow o\text{-}CH_3C_6H_4 \pm I) = (1.016 \pm 0.022) \log k(C_6H_5I \rightarrow C_6H_5 + I) - (0.031 \pm 0.054)$$

This leads to

$$k(o\text{-}CH_3C_6H_4I \rightarrow o\text{-}CH_3C_6H_4 + I) = 1.4 \times 10^{15} \exp(-33\,346/T)\ s^{-1} \text{ at } 1100\ K$$

Discussion

The rate expression for phenyl iodide decomposition that we have determined is in satisfactory agreement with that determined by Kominar, Krech, and Price.[2] Extrapolating our results to the lower temperature range where they carried out their experiments, we find $k(C_6H_5I \rightarrow C_6H_5 + I) = 0.19\ s^{-1}$ at 910 K. This can be compared with the value of $0.31\ s^{-1}$ as determined from the flow experiment. In absolute magnitude there is a discrepancy of a factor of 1.6. We are uncertain of the cause of this difference. It is our experience that the uncertainty in the rate constant from single-pulse shock-tube experiments is of the order of a factor of 1.3. It is possible that the flow experiments may have errors arising from uncertainties in the flow rates and reaction temperatures. There has been no previous studies on the decomposition of *o*-iodotoluene. Our studies establish that methyl substitution has virtually no effect in either a mechanistic or quantitative sense. Note that the rate constants at the reaction temperature for the phenyl iodide and *o*-iodotoluene decompositions are for practical purposes identical. It is suspected that the difference in rate expressions are to a large extent due to experimental errors. The smallness of the observed effect is somewhat surprising. In the decomposition of substituted alkanes[9] we have found that the effect of β-methylation can lead to changes of rate constants of a factor of 2 in the rate constant for C–C bond cleavage.

It is usually assumed that for such simple bond breaking reactions the activation energy is related to the bond dissociation energy at the reaction temperature through the relation ΔH(reaction) = ΔE(expt) + RT. Implicit in this relation is the assumption that the activation energy for the bond-forming process is zero in concentration units.[3] For phenyl iodide our results give ΔH(reaction) = 281.9 kJ at 1100 K. Since $\Delta H_f(C_6H_5I)$ = 117.6 kJ/mol[10] and $\Delta H_f(I)$ = 77.2 kJ/mol[11] at 1100 K, we find $\Delta H_f(C_6H_5)$ = 322.3 J/mol at 1100 K. Using the recently tabulated values[12] for the heat capacity of phenyl radical, where it is assumed that the only difference in the heat capacity of phenyl and benzene arises from the deletion of the vibrational frequencies associated with the hydrogen atom that has been removed from the latter, we find $\Delta H_f(C_6H_5)$ = 340.5 kJ/mol at 300 K. This is 12 kJ/mol higher than the value recently recommended by McMillen and Golden[4] of $\Delta H_f(C_6H_5) = 328.4 \pm 8$ kJ/mol. However, in view of an estimated uncertainty of 11 kJ/mol from our measurements, arising from a 6 kJ/mol uncertainty in the heat of formation of the phenyl iodide[10] and a 5 kJ/mol uncertainty from our measurements, the significance of this difference is unclear. It does raise the possibility that the C–H bond dissociation energy in benzene will have to be raised to 475.3 kJ/mol. On the other hand, the recommendation of McMillen and Golden[4] is not only based on the iodination studies[13] but also on the work of Chamberlain and Whittle[14] on the kinetics of the reactions $CF_3 + C_6H_6 \leftrightarrow C_6H_5 + CF_3H$, from which they obtained a heat of formation of the phenyl radical of 325 ± 8 kJ/mol. Since their procedure involved essentially a third-law analysis and we have verified their calculations, one would usually prefer such a value. However, the data[15] on the phenyl radical abstraction process (based on diphenylmercury photolysis) are not completely satisfactory. For example, their reported rate constant for phenyl radical attack on methane is a factor of 4 higher than that published in another study[16] that is based on acetophenone photolysis. Thus a consequence of our higher value for the heat of formation of the phenyl radical is the possibility that the very small data base on phenyl radical abstraction reactions may be subject to serious errors (close to an order of magnitude). The above is illustrative of the serious consequences that can arise in rate constants and equilibrium constants from what would appear to be small uncertainties in the heat of formation. Finally, for completeness we also mention the heat of formation of phenyl (300 K) as determined by Rosenstock et al.[17] of 330 ± 13 kJ/mol, from photoelectron–photoion coincidence mass spectrometry, and Kiefer et al.,[18] from high-temperature shock-tube studies, of 335 ± 8 kJ/mol. There is clearly room for more accurate determinations.

In spite of these uncertainties, our results can lead to an estimate of the reverse combination process between phenyl radicals and iodide atoms. The spread in the heat of formation of 12 kJ leads to an uncertainty in the results of a factor of 3. With the assumption of the entropies of the phenyl radical as tabulated by Burcat et al.,[12] if we use the heat of formation as recommended by McMillen and Golden we find a combination rate of 4.8×10^9 L/(mol·s), while for our higher heat of formation we arrive at a rate constant of 1.5×10^{10} L/(mol·s). The rate constant is thus very close to that for $CF_3 + Br$[19] but about an order of magnitude smaller than what we have found for alkyl and resonance-stabilized radicals with bromine and iodine atoms.[1]

Our failure to obtain a satisfactory mass balance at the lowest cyclopentane concentrations permits us to set an upper limit for the rate constant for phenyl radical attack on cyclopentane. Thus from our earlier analysis $kC = 6 \times 10^3\ s^{-1}$, where k is the rate constant for abstraction and C is the concentration of cyclopentane. The value of the latter is 1.2×10^{16} molecule/cm^3. This leads to

$$k(\text{phenyl} + \text{cyclopentane}) = 3 \times 10^8\ L/(mol{\cdot}s)$$

---

(9) Tsang, W. *J. Phys. Chem.* **1972**, *76*, 143.

(10) Stull, D. R. *Westrum*, E. F.; Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969; p 556. Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: New York, 1970.

(11) Stull, D. R.; Prophet, H. R. *JANAF Thermochemical Table*, 2nd ed.; US Government Printing Office: Washington, DC, 1971; NSRDS-NBS 37.

(12) Burcat, A.; Zelenik, F. J.; McBride, B. J. "Ideal Gas Thermodynamic Properties for the Phenyl, Phenoxy and *o*-Biphenyl Radicals", NASA Technical Memorandum 83880, National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH 44155; 1985.

(13) Rodgers, A. S.; Golden, D. M. *J. Am. Chem. Soc.* **1967**, *89*, 4578.

(14) Chamberlain, G. A.; Whittle, E. *Trans. Faraday Soc.* **1971**, *67*, 2077.

(15) Fielding, W.; Pritchard, H. O. *J. Phys. Chem.* **1962**, *66*, 821.

(16) Duncan, F. J.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1962**, 4672.

(17) Rosenstock, H. M.; Stockbauer, R.; Parr, A. C. *J. Chem. Phys.* **1980**, *73*, 773.

(18) Kiefer, J. H.; Mizerka, L. J.; Patel, M. R.; Wei, H. C. *J. Phys. Chem.* **1985**, *89*, 2013.

(19) Tsang, W. *J. Phys. Chem.* **1986**, *90*, 414.

at 1100 K. This is close to a factor of 30 higher than the extrapolated rate constant for methyl attack on cyclopentane. This difference may be somewhat diminished if we take into account the possibility of nonlinear Arrhenius behavior and the possibility of reaction occurring after the heating period. Nevertheless, the results are indicative of a very reactive phenyl radical. This is in line with the highly exothermic nature of the abstraction reaction.

Finally, although not directly related to the thrust of this work, we call attention to the abnormally large rate parameters for the decomposition of 1,2-dimethylcyclohexene in comparison to the reverse Diels–Alder decomposition of the monomethylated cyclohexene. The absolute rate is about a factor of 2.5 slower. A possible explanation for this observation is in terms of the increasing influence of a biradical mechanism.[20] Note that the rate expression for the breaking of the allylic C–C bond in 1-hexene is $8 \times 10^{15} \exp(-35\,600/T)$ s^{-1}.[21] The activation energy is very close to that which we obtained for 1,2-dimethylcyclohexene decomposition but 20 kJ higher than that for cyclohexene decomposition. The latter is known to be mostly a concerted process.

Acknowledgment. This work was carried out with the support of the Army Research Office under Contract MIPR 100-85.

Registry No. Phenyl iodide, 591-50-4; *o*-iodotoluene, 615-37-2; 1,2-dimethylcyclohexene, 1674-10-8; phenyl radical, 2396-01-2.

---

(20) Benson, S. W. *Thermochemical Kinetics*; New York, 1976.
(21) Tsang, W. *Int. J. Chem. Kinet.* **1978**, *10*, 1119.

Evidence for Two Electron States in Solvation and Scavenging Processes in Alcohols

M. A. Lewis[†] and C. D. Jonah*

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439 *(Received: February 18, 1986)*

The reactions of the precursors of the solvated electron were studied in 1-propanol and ethanol over a range of temperatures from −60 °C to room temperature using the Argonne stroboscopic pulse radiolysis system. For all scavengers, the decrease of the initial yield of the electron is temperature dependent. At −60 °C, these measurements show that an electron scavenger will decrease the initial yield of the electron and will also decrease the amount of absorption that grows in at 600 nm without changing the rate at which the grow-in occurs. The amount of decrease due to the electron scavenger is different for the initial yield and the fraction that grows in. These data are interpreted as showing two channels for solvation and two for reaction and that these channels depend on the energy of the electron and/or energy of the localization site.

There have been many studies documenting the reactivity of the electron species which precedes the solvated electron.[1-7] Originally, this species was identified as a dry or quasi-free electron, i.e., an electron immersed in a liquid, but subject only to long-range forces;[1,2] however, later studies, especially of alcohols at low temperatures, showed that the electron could also exist in a partially solvated or trapped state.[6,8] The existence of trapped electrons at room temperature has also been observed in several alcohols.[9,10] Thus, the term precursor as used to describe the electron which precedes the solvated electron is not one species but rather includes at least two states which are conceptually distinct but in fact are not sharply defined. In this study, we wish to learn more about these "precursors" and thereby obtain some insight into the energy loss mechanism and the reactivity of low-energy electrons.

In general, the energy loss mechanism depends on the energy levels of the molecules of the solvation.[11] Since the transition moments for processes involving ionization and electronic excitation are large, these processes account for most of the energy loss. Subexcitation electrons, those below the first excited state of the solvent, lose energy to the vibrational and rotational modes of the solvent, processes which are relatively inefficient. The end point of all these energy loss processes is the solvated electron. More specific information on the processes leading to the solvated electron exists. For instance, it has been established that there are two solvation channels: one that is fast and occurs in less that 15 ps and one that is slower and whose rate is temperature dependent. The latter solvation process involves the trapped electron, an intermediate species which absorbs light in the near-IR. Previous work in cold alcohols has shown that the electron's absorption spectrum evolved from the IR to the visible and that the rate of decay at 1300 nm was similar to the rate of growth at 600 nm.[6] This rate is characterized by a single exponential, τ_{sol}. It was further found that τ_{sol} could be correlated with τ_2 (the rotational relaxation time constant) and that τ_2 was correlated with the viscosity through the Debye equation.[8,10] Thus, the shift of the spectrum, or, equivalently, the slow solvation process detected in the visible, corresponds to e_{tr}^-, evolving to e_{sol}^- through the rotational relaxation of unassociated molecules.[6,8,10] The temperature dependence of the slow solvation rate parallels the temperature dependence of this viscosity.[9,10] However, the underlying mechanism which leads to these two different solvation pathways is not known.

The precursors are studied by measuring the initial yield of solvated electrons as a function of scavenger concentration, where the scavengers can be considered as probes.[1,11] (The effect of a scavenger molecule can be characterized by Q_{sol}, a measure of the ability of the scavenger to quench the formation of e_{sol}^-.) Q_{sol} is defined as the reciprocal of the concentration of the scavenger that is necessary to reduce the initial yield of the solvated electron to 1/e (37%) of the initial yield. (This quenching efficiency, Q_{sol}, is related to the previously defined C_{37} by $Q_{\mathrm{sol}} = 1/C_{37}$. Q_{sol} has the units of reciprocal concentration.) Q_{sol} can be extracted from experimental data in two different ways. If the initial yield follows an exponential dependence on scavenger concentration, then Q_{sol} is defined from Hunt's empirical relationship as[2]

[†] Present address: Chemical Technology Division, Argonne National Laboratory, Argonne, IL 60439.

(1) Wolff, R. K.; Bronskill, M. J.; Hunt, J. W. *J. Chem. Phys.* **1970**, *53*, 4211.
(2) Hunt, J. W.; Chase, W. J. *Can. J. Chem.* **1977**, *55*, 2080.
(3) Razem, D.; Hamill, W. H. *J. Phys. Chem.* **1978**, *82*, 1460.
(4) Razem, D.; Hamill, W. H. *J. Phys. Chem.* **1977**, *81*, 1625.
(5) Razem, D.; Hamill, W. H. *J. Phys. Chem.* **1978**, *82*, 488.
(6) Baxendale, J. H.; Wardman, P. *Faraday Trans. 1* **1973**, *69*, 584.
(7) Okazaki, K.; Freeman, G. R. *Can. J. Chem.* **1978**, *56*, 2313.
(8) Chase, W. J.; Hunt, J. W. *J. Phys. Chem.* **1975**, *79*, 2835.
(9) Kenney-Wallace, G. A.; Jonah, C. D. *J. Phys. Chem.* **1982**, *86*, 2572.
(10) Kenney-Wallace, G. A.; Jonah, C. D. *Chem. Phys. Lett.* **1976**, *39*, 596.
(11) Christophorou, L. G.; Compton, R. N. *Health Phys.* **1967**, *13*, 1277.

0022-3654/86/2090-5367$01.50/0 © 1986 American Chemical Society