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Mechanism and Rate of Hydrogen Atom Attack on Toluene at High Temperatures

D. Robaugh and W. Tsang*

Chemical Kinetics Division, National Bureau of Standards, Gaithersburg, Maryland 20899

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Hexamethylethane has been decomposed in the presence of large excesses of toluene and methane/toluene mixtures in single-pulse shock tube experiments in the temperature range of 950–1100 K and at 2–5 atm. Methane, ethane, isobutene, and benzene are the main light hydrocarbon reaction products. At sufficiently high toluene/hexmethylethane ratio (≥100 to 1) the main reactions are hexamethylethane $\rightarrow 2t\text{-}C_4H_9^\bullet$ (1); $t\text{-}C_4H_9^\bullet \rightarrow H^\bullet$ + isobutene (2); $H^\bullet + C_6H_5CH_3 \rightarrow C_6H_6 + CH_3^\bullet$ (4); $H^\bullet + C_6H_5CH_3 \rightarrow C_6H_5CH_2^\bullet + H_2$ (5). From the yields of isobutene and benzene, we find $k_5/k_4 = 9.8 \exp(-1560/T)$. In the presence of sufficiently large excess of methane, benzene yields are reduced. This is due to the competitive process $H + CH_4 \rightarrow CH_3 + H_2$ (7) and leads to $k_7/k_5 = 1.95 \exp(-2862/T)$. On the basis of $k_7 = 2.4 \times 10^{11} \exp(-7000/T)$ L/(mol s) (950–1100 K) we find $k_4 = 1.2 \times 10^{10} \exp(-2578/T)$ L/(mol s) and $k_5 = 1.2 \times 10^{11} \exp(-4138/T)$ L/(mol s). From the equilibrium constant, $k_{-4} = 1.2 \times 10^9 \exp(-8023/T)$ L/(mol s).

Introduction

This paper is concerned with the determination of the mechanisms and rates of hydrogen atoms attack on toluene at temperatures near 1000 K in a single-pulse shock tube. Previously, we have concentrated on unimolecular decompositions[1] and demonstrated that through the use of an internal standard highly accurate rate expressions can be obtained. We now extend the scope of such studies to cover bimolecular processes.

Hexamethylethane decomposition is used as a source of hydrogen atoms. The reactions are

$$\text{hexamethylethane} \rightarrow 2\textit{tert}\text{-butyl} \qquad (1)$$

$$\textit{tert}\text{-butyl} \rightarrow \text{isobutene} + \text{H (fast)} \qquad (2)$$

The newly formed hydrogen can now react with toluene which is present in large excess. There are four specific reaction channels

$$\text{H} + \text{toluene} \rightarrow \text{methylcyclohexadienyl} \qquad (3)$$

$$\rightarrow \text{methyl} + \text{benzene} \qquad (4)$$

$$\rightarrow \text{benzyl} + H_2 \qquad (5)$$

$$\rightarrow \text{methylphenyl} + H_2 \qquad (6)$$

Reactions 3 and 4 are related since the addition process can result in displacement. Under the present reaction conditions unless displacement occurs, there will be no net reaction since reaction 3 will be reversed. We will not be able to distinguish between the two abstraction modes, although it will be demonstrated subsequently that our results are compatible with the assumption that the abstraction of a benzylic hydrogen will be overwhelmingly favored. Our measurements will involve the determination of the concentrations of isobutene and benzene. The expression (isobutene/benzene) − 1 will under certain conditions be a direct measure of the relative importance of abstraction as compared to displacement. By carrying out additional studies with sufficiently large quantities of methane, we can use the decrease in benzene yield to relate the rates of H-atom attack on toluene to that on methane. Rate constants for the latter process are well established and will place the measurements on an absolute basis.

Table I contains the reuslts of previous investigations on the rate constants for the reactions of hydrogen atoms with toluene. Probably, the most pertinent information is the recent work of Rao and Skinner[2] on the induced decomposition of toluene-d_8. Their rate expression for hydrogen-atom abstraction of a benzyl hydrogen is the result of the coupling of their measurements which are in the 1300–1800 K range with the unpublished results of Ravishankara over the 600–1000 K range. We are uncertain how Ravishankara differentiated between abstraction and displacement.

TABLE I: Summary of Data Pertaining to the Reactions of Hydrogen Atoms with Toluene

H + toluene →	rate const, L/(mol s)	temp, K
benzyl + H_2 (2)	$7.6 \times 10^{-8} T^{6.5} \exp(-172/T)$	600–1700
benzene + CH_3 (est)	1.1×10^9	1050
products (4)	1×10^8	298
products (6)	$8 \times 10^{11} \exp(-4630/T)$	863–963
benzyl + H_2 (7) (est)	$3 \times 10^{10} \exp(-3000/T)$	1400
benzene + CH_3 (8)	$2 \times 10^9 \exp(-755/T)$	633

Nevertheless, the rate expression should give a maximum value of the rate constant at the applicable range. The $T^{6.5}$ dependence of the *A* factor is extraordinarily high and the rate expression does not reproduce the activation energy in the 600–1000 K range. The rate constant for displacement at 1050 K was an estimate based on Ravishankara's unpublished results on hydrogen abstraction from toluene and Price's[3] observation that methane to hydrogen ratio in toluene pyrolysis is 0.5. This is suggestive of a 2 to 1 ratio in favor of abstraction at 1000 K. However, possible contributions from surface processes in Price's work make this number uncertain.

The most reliable earlier study is the pulse radiolysis investigation of Sauer and Ward[4] at room temperature. The predominant process is addition, but displacement and abstraction can also make a contribution. Their measurements of hydrogen atom attack on toluene and benzene lead to a rate constant of 0.37×10^8 L/(mol s) for the latter or a factor of 2.8 smaller than that for reaction with toluene. This is in reasonable agreement with the value of 0.28×10^8 L/(mol s) from the rate expression given by Nicovich and Ravishankara[5]

$$k(H + C_6H_6 \rightarrow C_6H_7) = 4 \times 10^{10} \exp(-2170/T) \text{ L/(mol s)}$$

The results of Mkryan et al.,[6] although they are closer to our temperature regime, may not be as reliable since they are based on the analysis of a complicated reaction scheme. Benson and Haugen's[7] rate expression for the abstraction of a benzyl hydrogen from toluene must be considered a rough estimate, since they consider it as "typical" of a hydrogen abstraction process. The rate expression of Benson and Shaw[8] for the displacement of a methyl group from toluene by hydrogen is based on the assumption that hydrogen addition on the methyl site in toluene is equal to the rate of hydrogen addition to benzene (all sites) and the rate expression of Yang[9]

$$k(H^\bullet + C_6H_6 \rightarrow C_6H_7) = 1.26 \times 10^{10} \exp(-1963/T) \text{ L/(mol s)}$$

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[1] Tsang, W. *Shock Waves in Chemistry*; Lifshitz, A., Ed.; Marcel Dekker: New York, 1981; p 60.

[2] Rao, V. S., Skinner G. S. *J. Phys. Chem.* **1984**, *88*, 4362.

[3] Price, S. J. W. *Can. J. Chem.* **1962**, *40*, 1310.

[4] Sauer, M. C.; Ward, B. *J. Phys. Chem.* **1967**, *71*, 3971.

[5] Nicovich, J. M.; Ravishankara, A. R. *J. Phys. Chem.* **1984**, *8*, 2534.

[6] Mkryan, T. G.; Oganesyan, K. T.; Nalbandyan, A. B. *Arm. Chim. Zh.* **1972**, *25*, 893 (as quoted in: Kerr, J. A.; Moss, S. J. *Handbook of Bimolecular and Termolecular Reactions*; CRC Press: Boca Raton, FL, 1981; Vol. I, p 15.

[7] Benson, S. W.; Haugen, G. P. *J. Chem. Phys.* **1967**, *71*, 4044.

[8] Benson, S. W.; Shaw, R. *J. Chem. Phys.* **1967**, *47*, 4052. Benson, S. W.; Shaw, R. *J. Am. Chem. Soc.* **1967**, *89*, 5352.

[9] Yang, K. *J. Am. Chem. Soc.* **1952**, *84*, 3795.

Over the relevant temperature range the newer values for the rate constants are a factor of 3 larger. Benson and Shaw's rate expression, within the context of their postulated mechanism for the hydrogenolysis of toluene, fits the extensive data for this process very well; however, the scatter of data is such that it can easily accommodate rate constants a factor of 3 larger. The present situation with respect to hydrogen attack on toluene is thus uncertain. Particularly serious is the lack of definitive values for the branching ratio with regard to abstraction and displacement. The ratio is of consequence in any high-temperature situation where toluene is an important constituent since abstraction of a benzylic hydrogen will lead to a relatively inert benzyl radical while displacement will result in the formation of a highly reactive methyl radical.

Experimental Section

The experimental procedure used in this study is the same as in our earlier investigations[1] on alkane decomposition except that instead of paying attention only to the yields of the lighter unsaturates we now also make careful measurements on the benzene yield. Since we have previously[1] established that the rate expression for hexamethylethane decomposition is

$$k(\text{hexamethylethane} = 2\textit{tert}\text{-butyl}) = 3 \times 10^{16} \exp(-34490/T)/\text{s}$$

isobutene yields under certain conditions can be used as the internal temperature standard in the same manner as our unimolecular decomposition studies.[1] Gas chromatography with a silicone oil column and flame ionization detection is used for analysis. The hexamethylethane was obtained from Wiley Organics[10] and is of a stated purity of 99%. Gas chromatographic analysis did not reveal the presence of any impurities. Toluene of the highest purity was obtained from Philips Petroleum. A very small amount of benzene to the extent of 0.003% is apparently the principal impurity. This sets a lower limit to the amount of benzene that we can reliably detect from the displacement reaction. Except for vigorous degassing all the organics are used without further purification. The argon is of ultra-high-purity grade and is from Matheson.

Table II summarizes the mixtures and reaction conditions that have been used in these studies. The wide variations in absolute and relative concentrations are designed to determine the conditions under which accurate rate determinations can be made. The bimolecular reference reaction used in our determination of the rates of H-atom attack on toluene is the process

$$H^\bullet + CH_4 = CH_3 + H_2 \qquad (7)$$

with the rate expression $k = 2.4 \times 10^{11} \exp(-7000/T)$ L/(mol s). This reaction has been the subject of many studies over wide temperature ranges. The rate constants should be quite reliable.

Results

Product distribution from the shock-induced decomposition of hexamethylethane in the presence of large excesses of toluene include in order of relative amounts isobutene, benzene, methane, ethane, propylene, isobutane, and at higher extents of decomposition traces of allene and propyne. Extensive quantities of ethylbenzene and dibenzyl must also have been formed. These represent recombination products and can be formed after the heating period. We have not attempted to analyze for them. Their presence does not affect our conclusions except peripherally. The mechanism for the production of isobutene and benzene has been given earlier. Most of the methane must be formed from the process

$$CH_3^\bullet + C_6H_5CH_3 = CH_4 + C_6H_5CH_2^\bullet$$

TABLE II: Experimental Conditions (in 2–5 atm of Argon, 950–1150 K)

52.2 ppm hexamethylethane in 0.5% toluene
108 ppm hexamethylethane in 3% toluene
203 ppm hexamethylethane in 2.1% toluene
218 ppm hexamethylethane in 2.1% toluene and 12.2% CH_4
1979 ppm hexamethylethane in 2.3% toluene

Ethane is formed from the combination of methyl radicals. It is always formed in significantly smaller quantities than methane. As would be expected from such a mechanism, the relative amounts of methane to ethane decreases as the methyl radicals in the system increases. The total amount of methane and ethane expressed as number of methyl groups is usually 60–80% of the benzene found. The difference is indicative of the contribution from the combination of benzyl and methyl radicals. Propylene yields are about 3% of those of isobutene. We beliave this represents a minor channel from *tert*-butyl radical decomposition. Presumably it is a consequence of 1,2 hydrogen shift followed by the decomposition of the isobutyl radical. The very small amounts of isobutane formed (less than 1%) are probably due to a molecular decomposition process of hexamethylethane.[13] The allene and propyne that are found are due to the induced decomposition of isobutene itself. Qualitatively, all of the products can be accounted for and the relative amounts found are in accord with the postulated mechanism.

Initial quantitative studies are designed to determine the conditions under which it will be possible to obtain the optimum rate constants or rate expressions and lead to the determination of the correction factors that will optimize the quantitative results. Figure 1 shows data illustrating the effect of hexamethylethane to toluene ratio. The data are plotted in terms of isobutene to benzene yields against total yields of benzene. It is designed to illustrate the relative rates of hydrogen attack on toluene as compared to that on hexamethylethane. Benzene yield is used as the *x* axis since to a certain extent it is a measure of hexamethylethane decomposition via C–C bond cleavage. The assumed mechanisms are

$$H^\bullet + C_8H_{18} = C_8H_{17}^\bullet + H_2 \qquad (8)$$

$$C_8H_{17}^\bullet = i\text{-}C_4H_8 + t\text{-}C_4H_9^\bullet$$

and

$$t\text{-}C_4H_9^\bullet = i\text{-}C_4H_8 + H^\bullet$$

The effect of H attack on hexamethylethane is to create two extra isobutenes. Isobutene yields are thus not a measure of C–C bond cleavage in hexamethylethane. The concentration of hydrogen atoms is however conserved. Thus benzene yield is uneffected by induced hexamethylethane decomposition. On this basis the data in Figure 1 demonstrate that when the quantity of hexamethylethane is increased, as expected, isobutene yields also increased. It is also clear that when the ratio of hexmethylethane to toluene approaches the 100 to 1 value the contribution from the induced decomposition becomes very small. Indeed, our results would suggest that for present purposes at 300 to 1, all contributions from the induced decomposition of hexamethylethane will have disappeared. As noted earlier, the small quantities of benzene that are present as an impurity set an upper limit with respect to the toluene to hexamethylethane ratio that can be tolerated. Thus most of the quantitative measurements are carried out with the 100 to 1 toluene to hexamethylethane ratio, and a 3% correction factor was made to the isobutene yields in order to account for the induced decomposition. Figure 2 contains results illustrating the effects of total concentration. What is required is that the system contains sufficient toluene so that every hydrogen atom that is formed from *tert*-butyl radical decomposition has an opportunity to attack a toluene molecule. It would appear that at concentrations equivalent to 0.5% toluene, we are beginning to diverge from the required quantitative conversion. As a result, all our quantitative studies were carried out with concentrations of toluene at 2% or more. Note that a hydrogen atom that survives

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[10] 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 necessarily the best available for the purpose.

[11] Clark, T. C.; Dove, J. E. *Can. J. Chem.* **1973**, *51*, 2147.

[12] Shaw, R. *J. Phys. Chem.* Ref. *Data* **1978**, *7*, 1979.

[13] Atri, G. M.; Baldwin, R. R.; Evans, G. A.; Wacher, R. W. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 366.

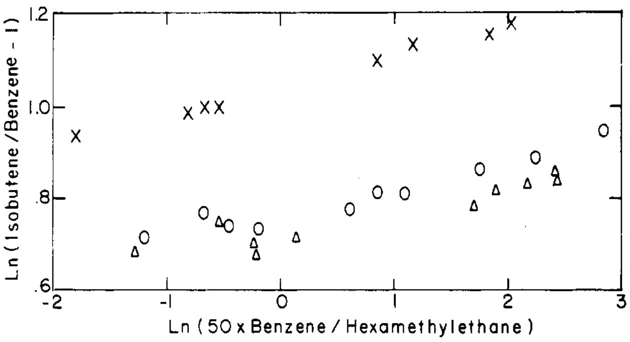

Figure 1. Effect of varying toluene to hexamethylethane ratio on abstraction to displacement rate ratio, as a function of benzene yields (pressure, 2–5 atm of argon): ×, 1979 ppm hexamethylethane in 2.3% toluene; ○, 218 ppm hexamethylethane in 2.1% toluene; △, 108 ppm hexamethylethane in 3% toluene.

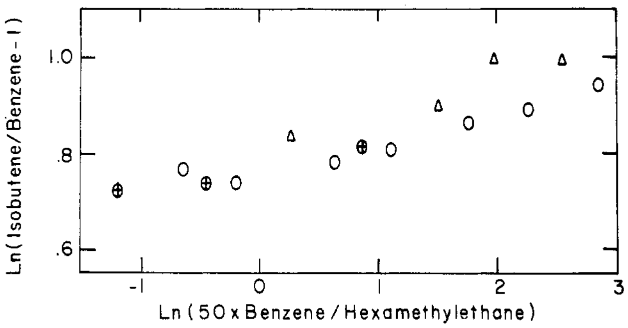

Figure 2. Effect of varying concentration levels of toluene on abstraction to displacement ratio, as a function of benzene yield (~2.5 atm of argon and toluene/hexamethylethane = 100): △, ~7.5 Torr of toluene; ○, ~30 Torr of toluene; ⊕, ~60 Torr of toluene.

the heating period will have the possibility of adding on to the aromatic moiety and thus distorting the results. Finally, the reaction

$$H^{\bullet} + C_6H_5CH_2^{\bullet} \rightarrow C_6H_5CH_3 \qquad (9)$$

is an alternative sink for hydrogen atoms. The general trend of our data as summarized in Figures 1 and 2 suggest that with the mixtures we will be using for our quantitative conclusions this should not have any significant effect. However, the deviations from the limiting rates may have contributions from this source.

The data are analyzed via comparative rate techniques. This is done in two stages. First we determine the relative rate constants for abstraction ($k_5 + k_6$) and displacement (k_4). We then relate these rate constants to that for hydrogen atom attack on methane. Since the latter is well established, this puts all our numbers on an absolute basis.

For the former, the ratio of the rate constants for abstraction compared to that for displacement $(k_6 + k_5)/k_4$ is equal to the experimentally determined quantity, (isobutene/benzene) − 1, for those experiments where all the hydrogen atoms released into the system react with toluene. When this is coupled with the rate constant for hexamethylethane decomposition

$$k_1 = \ln\,(1 - \text{isobutene}/2(C_8H_{18}))/t$$

where t is the residence time and is of the order of 500 μs, and the data are plotted against each other, the results can be seen in Figure 3, curve A. They lead to the relationship

$$\log\,((k_6 + k_5)/k_4) = (0.045 \pm 0.004)\log k_1 + (0.275 \pm 0.009)$$

Substituting into this relation the value for k_1 given above, we obtain

$$(k_6 + k_5)/k_4 = 9.8\exp(-1560/T)$$

When large quantities of methane are added to the reaction mixture, there will be corresponding decreases in the benzene yield. The abstraction to displacement ratio, (isobutene/benzene) − 1, is now equal to the expression $((k_6 + k_5)(C_7H_8) + k_7(CH_4))/k_4(C_7H_8)$. Treating the results in the same manner as above leads to curve B in Figure 3. The rate relationship is then

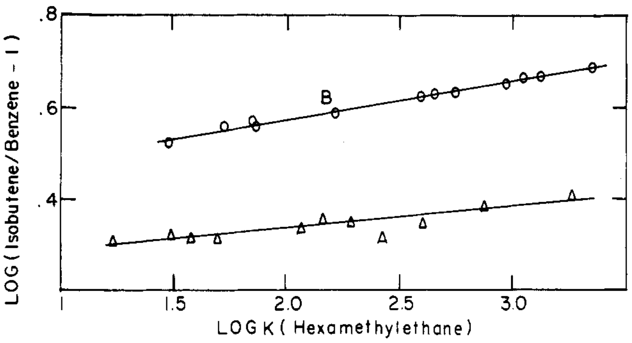

Figure 3. Comparative rate study on abstraction to displacement rate ratio vs. extent of hexamethylethane decomposition: ○, 203 ppm hexamethylethane, 2.1% toluene, 12.2% CH_4; △, 218 ppm hexamethylethane, 2.1% toluene, in 2–5 atm of argon, 950–1150 K.

$$\log\,((k_6 + k_5)(C_7H_8) + k_7(CH_4)/k_4(C_7H_8)) = (0.083 \pm 0.003)\log k_1 + (0.410 \pm 0.007)$$

Taking the difference between these two comparative rate expressions and then making a best linear fit of the logarithm of the ratio of abstraction rate constants with the rate constant for hexamethylethane bond breaking lead to the relation

$$\log\,(k_7(CH_4)/(k_5 + k_6)(C_7H_8)) = 0.083\log k_1 - 1.08$$

Upon substitution of the relative amounts of toluene and methane in the system, we obtain

$$k_7/(k_5 + k_6) = 1.95\exp(-2862/T)$$

Using the rate expression for hydrogen atom attack on methane $k_7 = 2.4 \times 10^{11}\exp(-7000/T)$ L/(mol s), given earlier, we than obtain the following absolute values for the rate constants

$$k_4 = 1.2 \times 10^{10}\exp(-2578/T)\ \text{L/(mol s)}$$

$$k_6 + k_5 = 1.2 \times 10^{11}\exp(-4138/T)\ \text{L/(mol s)}$$

over the temperature range of 950–1100 K and $k_8 \sim 5 \times 10^9$ L/(mol s) at 1032 K. The dependence of these values on the rate constant for the H + CH_4 must be borne in mind. Due to the uncertainty in the curvature of the Arrhenius plot, there may be problems with respect to the rate expression we use. The equation given here is based on the analysis of Clark and Dove[11] and Shaw.[12] They suggested the rate expressions

$$k_7 = 22.4T^3\exp(-4406/T)\ \text{L/(mol s) and}$$

$$1.41 \times 10^4T^2\exp(-4449/T)\ \text{L/(mol s)}$$

The former seems to fit the data at the highest temperature better. On the other hand, writing the rate expression with a power law dependence for the preexponential factor is purely a matter of convenience. Transition-state considerations suggest an increasingly stronger temperature dependence as the temperature increases. Our rate expression at 1000 K is therefore based on a $T^{2.5}$ dependence of the preexponential factor and a rate constant at 1000 K that is intermediate between the predictions of Clark and Dove and Shaw. We estimate that this will lead to a possible uncertainty of 30% in the rate constant and 4 kJ in the activation energy.

The data on Figure 1 also lead to a rough value of the relative rates of H-atom attack on toluene and hexmethylethane. Over the range of our experiments the abstraction to addition ratio is increased by a factor of 1.4 when the ratio of toluene to hexamethylethane is decreased from 300 to 1 to 11.5 to 1. The magnitude of this difference is too small for a determination of the temperature dependence. However, the absolute magnitudes especially at the lower extent of reaction should be quite reliable. On this basis we obtain

$$2k_8(C_8H_{18})/(k_5 + k_6)(C_7H_8) = 0.4 \pm 0.05$$

where the factor of 2 takes into account the two isobutenes formed for every H atom destroyed in this manner. Substituting into the above the hexamethylethane to toluene ratio of 11.5, we get

$$k_8/(k_5 + k_6) = 2.3 \pm 0.25$$

In terms of rates relative to H-atom abstraction from methane at 1032 K, a temperature that is in the midpoint of our range, we find $k_7{:}k_6 + k_5{:}k_8$ is equal to 1:8:~18. On a per H-atom basis and assuming that k_5, H-atom abstraction from the ring, makes an insignificant contribution leads to the ratio 1:10:~3.7. Finally, the total rate constant for H-atom disappearance during attack on toluene is

$$k_4 + k_5 + k_6 = 1 \times 10^{11} \exp(-3630/T) \text{ L/(mol s)}$$

This is the expression that can most readily be compared with direct studies measuring H-atom disappearance.

Discussion

The rate constants deduced for the displacement of methyl group in toluene by hydrogen is in excellent agreement with the values obtained from the expression given by Rao and Skinner and Benson and Shaw. The latter is fortuitous since the kinetic data they used have now been superseded by more accurate determinations. Nevertheless, our results do validate Benson and Shaw's mechanism for the hydrogenolysis of toluene. From our results, the rate expression for toluene hydrogenolysis is $6 \times 10^{11} \exp(-28300/T)$ (L/(mol s))$^{1/2}$. Within the scatter of the extensive data this is indistinguishable from their expression of $1.2 \times 10^{11} \exp(-26900/T)$ (L/(mol s))$^{1/2}$.

Our results are in disagreement with Benson and Shaw's conclusion regarding the equality of the rate constants for hydrogen addition to benzene and to the methyl site in toluene. In the present analysis using the expression of Nicovich and Ravishankara for the former, we find, since our activation energy or displacement is very close to theirs for addition, that over the entire applicable range the difference is of the order of 4–6. It appears that methyl substitution has very little effect on the reactivity of that particular site. This is exactly the same conclusion as that of Rao and Skinner which is based on Ravishankara's unpublished results on hydrogen addition to toluene and Price's ratio of 0.5 for CH_4/H_2 yields. Our comparable value at 1032 K is 0.45 as derived from the quantity (isobutene/benzene) − 1. The results of Sauer and Ward at room temperature show that H attck on toluene is a factor of 2.4 times faster than H attack on benzene. Clearly some of the neighboring sites on the aromatic ring are being rendered more active. All of the above must be tempered by the fact that we are extrapolating 1000 K results to 700 K (Benson and Shaw). However, the magnitude of the temperature dependence of the A factor would have to be extremely large in order to fit all the results.

The limiting rate expression of Nicovich and Ravishankara for the abstraction of H atoms from the benzene ring leads to rate constants that are a factor of 30 lower than our total rate constant for abstraction. The inference is overwhelming that what we have measured is essentially the rate constant for the abstraction of benzylic hydrogen. Our rate expression is in excellent agreement with the unpublished results of the Ravishankara as reported by Rao and Skinner. The estimated rate expression of Benson and Haugen is within a factor of 1.5 of our measured number at 1032 K. Our measurements suggest that the benzyl resonance energy is not completely manifested in the activation energy for abstraction. Coupling this with a drop in the A factor, it means that the rate constants at 1000 K are probably close to that for H abstraction by hydrogen from substituted alkanes. Quantitatively, the activation energy barrier in going from methane to toluene is lowered by only 24 kJ/mol despite a change in reaction exothermicity of 63 kJ. No Polanyi type plots will encompass such data. A change of this magnitude will have, however, considerable significance at lower temperatures.

Our experimental results suggest a rate constnat of approximately 3×10^9 L/(mol s) for the rate of hydrogen atom attack on toluene at our reaction temperatures. This is a factor of 4 larger than the results of Mkryan et al. Considering the complexities of the system they studied the agreement must be considered to be satisfactory. Our results also permit a check to be made on the effectiveness of toluene in capturing all the hydrogen atoms that are released into the system. The relevant relation is

$$\text{fraction captured} = 1 - ((1 - \exp(-kct))/kct)$$

where k is the total rate constant for H-atom reaction, c is the concentration of toluene, and t is the residence time of about 500 μs. For studies with 0.5% toluene, 100 to 1 hexamethylethane to toluene ratio at 3 atm, we find kct to be of the order of 100. This implies over 99% conversion. On this basis we are forced to attribute the small increase in the (isobutene/benzene) − 1 value as seen in Figure 2 to the interaction between H atoms and the benzyl radicals in the system. Furthermore, the absence of a strong dependence on the extent of reaction suggests that benzyl radicals may be lost through recombination. This opens up interesting possibilities for subsequent work. It has no consequences in the present context, since all our quantitative results are based on studies at higher concentrations.

An interesting check of our results can be made by a comparison of our measured rate constant for H-atom attack on hexamethylethane with the literature value for the same reaction with ethane. Since both reactions involve primary hydrogens, we expect a rough correspondence in rate constants on a per hydrogen basis. This is indeed the case. At 1032 K, present results lead to a rate constant per hydrogen atom of 2.7×10^8 L/(mol s) while the evaluation of H + ethane by Dove and Clark[11] gives 2.6×10^8 L/(mol s). The exact agreement is fortuitous since the uncertainty in the latter is a factor of 1.5 and we have earlier estimated the uncertainty in the rate constant for the H + CH_4 reaction to be 30%. Indeed, we suspect that our rate constant ratio of 1 to 3.7 for H attack on a methane hydrogen and a primary hydrogen atom with an estimated uncertainty at 20% is the best presently available. Thus, the general technique has great potential in deriving a very accurate set of internally self-consistent values for H-atom processes at high temperatures. The possible extensions to other radical molecule reactions are obvious.

The possibility of hydrogen atoms reacting with hexamethylethane and benzyl radicals gives a very good explanation for the high temperature dependence of the A factor for hydrogen abstraction given by Rao and Skinner. In this study, they generated H atoms from neopentane in a mixture where toluene is present only in fourfold excess. In our studies with a tenfold excess of toluene compared to hexamethylethane there is a 40% excess production of isobutene compared to the situation where we are reasonably sure that all the hydrogen atoms are reacting with the toluene. Even allowing for the smaller number of available hydrogen in neopentane it is likely that they have overestimated their rate constant for hydrogen abstraction from benzene by close to a factor of 2. This change would result in a reduction of the temperature dependence of the A factor to T^2–T^3. This seems to be in a more likely range.

Finally, through detailed balance, we arrive at the expression $k(CH_3^\bullet + C_6H_6 \rightarrow C_6H_5CH_3 + H^\bullet) = 1.2 \times 10^9 \exp(-8023/T)$ L/(mol s) at 1000 K for the displacement of a hydrogen atom from benzene by methyl. This rate expression should have the same reliability as the experimentally determined rate constant for the reverse reaction since the thermodynamics is accurately known. It can be compared with the recommended expression for the abstraction of an H atom by methyl from benzene.[14]

$$k(CH_3^\bullet + C_6H_6 \rightarrow CH_4 + C_6H_5^\bullet) \sim 3 \times 10^8 \exp(-5590/T) \text{ L/(mol s)}$$

At 1000 K the former is only a factor of 3 smaller. Thus at higher temperatures methyl radicals provide a pathway for the growth of a side chain on benzene. These have interesting consequences in a high-temperature pyrolysis system. Note that the displace-

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(14) Kerr, J. A.; Parsonage, M. J. *Evaluated Kinetic Data on Gas Phase Hydrogen Transfer of Methyl Radicals*; Butterworth: Boston, MA, 1976; p 79.

ment reaction is actually a composite process. The individual steps are

$$\mathrm{CH_3} + \mathrm{C_6H_6} \underset{\mathrm{b}}{\overset{\mathrm{a}}{\rightleftarrows}} \text{methylcyclohexadienyl} \xrightarrow{\mathrm{c}} \mathrm{H} + \text{toluene}$$

In terms of elementary reactions, the rate constant is

$$k_8(\mathrm{CH_3} + \mathrm{C_6H_6} \rightarrow \mathrm{H} + \text{toluene}) = k_\mathrm{a}(k_\mathrm{c}/(k_\mathrm{b} + k_\mathrm{c}))$$

If we assume that $k_\mathrm{c}/k_\mathrm{b}$ is equal to the ratio of rate constants for the decomposition of *sec*-butyl radical to propylene and the 2-butenes,[15] then

$$k_\mathrm{a} \cong 2.9 \times 10^9 \exp(-5600/T)\ \mathrm{L/(mol\ s)}$$

Unfortunately, there are no low-temperature measurements on the rate constants of the reaction that can be used for comparison. The rate parameters are however larger than for methyl additions to olefins.

Registry No. $\mathrm{C_6H_5CH_3}$, 108-88-3; H, 12385-13-6.

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CONDENSED PHASES AND MACROMOLECULES

Dielectric Constant near the Liquid–Liquid Critical Point in Perfluoromethylcyclohexane + Carbon Tetrachloride

R. H. Cohn and S. C. Greer*

Department of Chemistry and Biochemistry, The University of Maryland at College Park, College Park, Maryland 20742 *(Received: February 12, 1986; In Final Form: April 3, 1986)*

We have measured the static dielectric constant, ϵ, as a function of temperature for a mixture of perfluoromethylcyclohexane + carbon tetrachloride which was near the critical composition. The measurements extend over the temperature range $6.6 \times 10^{-6} < t < 5.5 \times 10^{-2}$, where t is the reduced temperature $(T - T_\mathrm{c})/T_\mathrm{c}$, T is the temperature, and T_c is the critical temperature (302.223 K). The data are consistent with the theoretical prediction of a temperature-dependent term due to critical fluctuations which has a critical exponent $(1 - \alpha)$, where α is 0.11. For most other critical liquid mixtures for which $\epsilon(t)$ has been studied, $\epsilon(t)$ shows a *decrease* near T_c, below an extrapolation of the "background" behavior. For this mixture, however, the critical fluctuations cause an *increase* in $\epsilon(t)$ near T_c which is very small, barely greater than the resolution of the experiment. It is possible that the increase reflects the behavior of the density, rather than the inherent anomaly in ϵ.

Introduction

The large fluctuations which develop in a fluid near a critical point affect the thermodynamic properties, including the static dielectric constant, ϵ. Thermodynamic[1,2] and microscopic[3,4] theories have been developed for the behavior of the dielectric constant near a liquid–gas or liquid–liquid critical point. The expected functional form is

$$\epsilon/\rho = A_1 + A_2 t + A_3 t^{(1-\alpha)} + A_4 t^{(1-\alpha+\Delta)} + \ldots \qquad (1)$$

where ρ is the density, $t = (T - T_\mathrm{c})/T_\mathrm{c}$ is the reduced temperature, T is the temperature, T_c is the critical temperature, α is the critical exponent for the heat capacity[5] (at constant volume at a liquid–vapor critical point and at constant pressure and composition at a liquid–liquid critical point), and Δ is the correction-to-scaling exponent.[6,7] The most recent calculations find $\alpha = 0.11$ and $\Delta = 0.50$.[8] At a liquid–gas critical point, measurements of ϵ are made at constant density. For a liquid–liquid critical point, measurements of ϵ are made at constant pressure and the density on the left side of eq 1 is not a constant; in fact, the density also has a $(1 - \alpha)$ critical term and must be included in eq 1 in order to assess unambiguously the behavior of $\epsilon(t)$.[1]

We note that the effect of the $(1 - \alpha)$ term is the addition or subtraction of a term, the magnitude of which decreases as $t \rightarrow 0$; thus, a *positive* sign for A_3 will cause an apparent *decrease* in $\epsilon(t)$ below "background" as T_c is approached and a *negative* A_3 will cause an increase in $\epsilon(t)$ near T_c. The thermodynamic arguments of Sengers et al.[1] and Mistura[2] predict that A_3 should have the opposite sign from that of $\mathrm{d}T_\mathrm{c}/\mathrm{d}E^2$, where E is the electric field. The two measurements which have been reported for $\mathrm{d}T_\mathrm{c}/\mathrm{d}E^2$ (for 2,2,4-trimethylpentane + nitrobenzene[9] and for aniline + cyclohexane[10]) both find $\mathrm{d}T_\mathrm{c}/\mathrm{d}E^2$ to be negative, which requires A_3 to be positive, which leads to a decrease in ϵ near T_c. Shakhparonov[11] has argued that the effect of fluctuations in a fluid is to decrease its dielectric constant; Lomova and Shakhparonov[12] add that while this decrease is expected near an upper critical point, an increase would be expected near a lower critical point.

There is a school of thought that the anomaly in the dielectric constant should have the same critical exponent as does that in the electrical resistivity.[13] Measurements of the resistivity at liquid–liquid critical points in nonaqueous mixtures[14] frequently yield the exponent $2\beta = 0.65$, where β is the exponent describing the coexistence curve,[5] rather than $(1 - \alpha)$. In two cases, the mixtures isobutyric acid + water and phenol + water, the resistivity has a $(1 - \alpha)$ anomaly.[15]

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