JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 98, NUMBER 3 FEBRUARY 4, 1976

Diffusion in Liquids. II. The Dependence of the Diffusion Coefficients on Molecular Weight and on Temperature

Eli Grushka* and Edward J. Kikta, Jr.

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214.

Received February 7, 1975

Abstract: The diffusion coefficients of 12 phenones, ten with straight alkane side chains and two with branched chains, were measured at five temperatures ranging from 40 to 80°C. It is found that, as the molecular weight increases, the diffusion coefficient decreases. A linear relationship is found between D_{AB} and the increment in the relative molecular weight increase $(M_2 - M_1)/M_1$. The temperature dependence of the diffusion coefficients was studied and a linear correlation between either log D_{AB} and $1/T$ or D_{AB} and T was found. If the rate equation is used, one can assume that each CH_2 group contributes 73 cal to the activation energy. Using the fluidity approach, it is seen that extrapolation of D_{AB} vs. T plots to zero diffusion yields different limiting temperatures, T_0, for each phenone.

The theoretical treatment of transport properties in liquid systems is not as well developed as in gases. The infinite dilution diffusion coefficient, D_{AB}, of solute A in solvent B is interpreted frequently in terms of Einstein's equation[1] or in terms of Eyring's rate theories.[2] Kirkwood and his co-workers (see ref 3 and references therein) dealt with diffusion from a statistical mechanical point of view. The theories of irreversible thermodynamics were used by several workers. A brief but critical review of these approaches was given recently by Ghai, Ertl, and Dullien.[4] Utilizing Batschinski's arguments[5] Hildebrand (e.g., ref 6 and 7) recently discussed viscosity and diffusion from a fluidity point of view, and a modification of this concept was suggested by Ertl and Dullien.[8] More recently, various hard sphere models based on Enskog's work were used by, among others, Alder and his co-workers (e.g., ref 9 and references therein), Chandler (e.g., ref 10 and references therein), and Dymond (ref 11 and references therein). Chandler[10] was particularly successful in treating molecular liquids as rough hard sphere fluids. It is fast becoming apparent that this approach is most promising. For example, DeZwaan and Jonas[12] have recently used the model in their analysis of high pressure NMR data. To date, the hard sphere model was applied mainly to self-diffusion of relatively small molecules such as CCl_4. In addition, in order to reproduce or estimate the molecular behavior of liquids, high pressure studies are needed since density changes are most important. Alder and co-workers[9] did utilize the model in studying binary diffusion of solutes which are smaller in size and in mass than the solvent. The theoretical prediction, although very encouraging, did show some deviation from experimental data.

In actual practice one is frequently more interested in diffusion in mixtures rather than self-diffusion, and in the dependence of the diffusion coefficients on the temperature rather than on the pressure. Equally as important is the dependence of the (binary) diffusion coefficient on the size and shape of the diffusing species.

A survey of the literature concerning diffusion in liquid systems points out the fact that (a) most studies were aimed at determining the effect of the concentration of the diffusing species, and (b) most studies were carried out at only one or two temperatures. Bird et al.[13] and Hildebrand[6] commented on the lack of systematic studies of diffusion behavior. Perhaps this lack of information was due mainly to the experimental difficulties in amassing large quantities of reliable data in a reasonable time. The recent emergence of a dynamic method of measuring diffusion coefficients, based on Taylor's work[14,15] might help in obtaining the diffusion coefficients needed for such studies. Ouano,[16] Pratt and Wakeham,[17] Grushka and Kikta,[18] Komiyama and Smith,[19] Jhaveri et al.,[20] and Ouano and Carothers[21] have all shown that the rate of accumulation of precise, and presumably accurate, diffusion coefficient data can be increased many fold using the dynamic method (the so-called "chromatographic broadening technique").

The work described here was designed to test the dependence of the diffusion coefficients on the molecular size and on the temperature. Changing the temperature will also affect the density of the solvent and, therefore, rigorous hard sphere calculations cannot be done on the following sets of data. It should be noticed, however, that Alder and Hildebrand[22] indicate that the fluidity concept can lead to the calculation of self-diffusion of hard sphere fluids. Hilde-

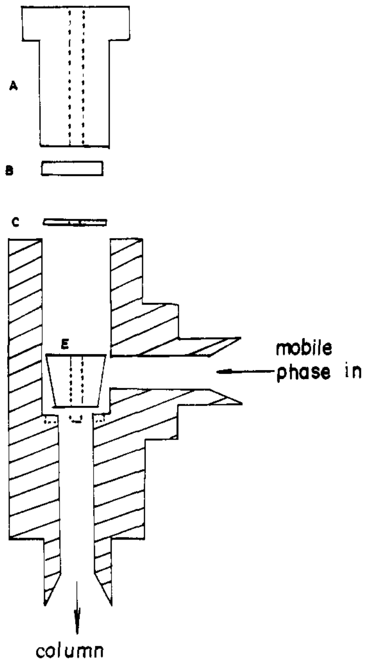


Figure 1. Improved injection head used in this study: (A) 1/16 in. s. s. Swagelok male fitting, (B) septum, (C) washer, (D) 1/16 in. brass union T, (E) 1/16 in. brass front ferrul.

brand's equation for self-diffusion is given as

$$D = B\frac{V - V_0}{V_0} \tag{1}$$

where B is a constant, V is the molar volume, and V_0 is the volume at which viscous flow ceases. Equation 1 indicates a linear relationship between D and T. Ertl and Dullien[8] found that the modification

$$D = B'\left(\frac{V - V_0}{V_0}\right)m \tag{2}$$

where m is a constant, fitted their data much better than eq 1, and that in any event both equations do not hold for reduced temperature T_r (i.e., T/T_c, where T_c is the critical temperature) below 0.46. Cullinan and Kosanovich[23] gave further evidence regarding to the invalidity of eq 1 at $T_r <$ 0.46.

With regard to the size of the diffusant there are many reports in the literature showing that for a nonassociated system, the diffusion coefficient, D_{AB}, at a given solute concentration, is dependent on the size of the solute (viz., ref 24, 25, 26). However, most of these studies were (a) carried out at one temperature or (b) are based on data from several laboratories or (c) did not include a large range of molecular weights.

We report here the diffusion coefficients of 12 phenones and benzene in heptane at 40°, 50°, 60°, 70°, and 80°C. The phenones where chosen mainly because the aromatic ring facilitated the detection of the species.

Experimental Section

Apparatus. The experimental apparatus was similar to that described before[18] with the following changes. (1) The capacity of the solvent delivery system was increased to ensure longer continuous operation time. (2) The data were recorded with a Beckman 10 in. Model 1005 chart recorder. (3) The injection head designed was changed as follows. The top threaded portion of a 1/16 in. Swagelok union T was removed. The remainder of this arm of the T was drilled to a diameter just slightly smaller than 1/16 in. The drilled hole extended to just below the side arm of the union T. Two cross slots were cut across the bottom of the enlarged opening. A 1/16 in. brass Swagelok front ferrul was placed in the drilled portion in such a manner that the narrow part of the ferrul rested on the slotted part. The function of the ferrul was to guide the syringe needle during the solute injection. The slots allowed the liquid mobile phase (the solvent) to flow into the diffusion tube unobstructed by the ferrul. A stainless steel washer was put on the ferrul to support the septum. A stainless steel 1/16 in. male Swagelok GC fitting, similar to a cap, which has been drilled to allow injection, acted as a self-tapping screw into the brass body of the modified union T and a properly threaded seal resulted. The seal did not leak at inlet pressures in excess of 1000 psi (the actual work was done with inlet pressure of about 10 psi).

Table I. Diffusion Coefficients of Benzene at Infinite Dilution in *n*-Heptane at Several Temperatures

	$10^5 D_{AB}$ (cm²/s)			
Temp °C	This study	Wilke–Chang (ref 29)	Sanni et al. (ref 27)	Calus and Tyn (ref 28)
40	4.45	4.39	4.74	4.30
50	5.05	4.90	5.33	4.95
60	5.51	5.53	5.90	5.61
70	6.31	6.26	6.49	6.25
80	7.00	7.15	7.07	6.90

Since the mobile phase was heptane, a suitable septum was neoprene rubber. Most other rubbers or plastic polymers tended to swell or become very soft when in contact with heptane. Teflon could not be used since it tended to shred after several injections and block the diffusion tube or the detector cell.

Reagents. The heptane was spectroanalyzed grade brought from Fisher Scientific. The phenones and benzene were purchased from various manufacturers. All were of purity greater than 99%.

Procedure. It was found that in order to obtain consistent results, the septum had to be thoroughly washed and boiled several times in heptane. Otherwise, at high temperatures, the heptane would leach out some uv absorbing material from the septum, and severe baseline drifts were observed.

At each temperature, 10 μl of a heptane solution containing 100 μg of the component of interest was injected, with a Glenco syringe, directly into the diffusion tube. At least three injections were made for each component at each temperature. Successive injections were made in the manner described previously.[18] The recorder chart speeds were carefully calibrated, and so adjusted that the width of the eluted peaks were several centimeters. This reduced the error in measuring peak width.

Results and Discussion

Major sources of error involved in the method were discussed previously.[18] Data reduction was done directly from the recorder trace and did not involve the computer manipulation as used by Pratt and Wakeham[17] or Ouano and Carothers.[21] The reproducibility of the data, as shown in Table II, was quite satisfactory for the present study.

A complete mathematical description of the method can be found elsewhere.[14–21] It is sufficient to indicate here that the diffusion coefficients are experimentally obtained from the expression

$$D_{AB} = \frac{0.2310 r^2 U t_R^2}{L W_{1/2}^2} \tag{3}$$

L is the column length, t_R is the residence time of the solute in the tube, U is the solvent velocity, r is the radius of the tube, and $W_{1/2}$ is the eluted peak width at half its height.

To check the accuracy of the method, the diffusion coefficient of benzene in heptane was obtained and compared with the results of Sanni et al.[27] and of Calus et al.[28] The data are shown in Table I. Also shown are the predicted values using the Wilke-Chang equation.[29] The data of Sanni et al. were extrapolated up to 80°C. As Table I shows the present data fall between the two literature references. The agreement with the Wilke-Chang equation is rather

Table II. Diffusion Coefficient × 10^5 cm^2/s for Phenones in *n*-Heptane at Infinite Dilution

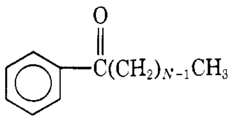
Compound	40°C	50°C	60°C	70°C	80°C
Acetophenone	2.26 ± 0.04	2.60 ± 0.02	2.97 ± 0.03	3.36 ± 0.01	3.94 ± 0.04
Propiophenone	2.16 ± 0.01	2.37 ± 0.05	2.79 ± 0.03	3.13 ± 0.02	3.66 ± 0.01
n-Butyrophenone[a]	2.08 ± 0.01	2.14 ± 0.01	2.58 ± 0.01	2.70 ± 0.03	3.29 ± 0.01
Isobutyrophenone	2.02 ± 0.03	2.09 ± 0.02	2.39 ± 0.02	2.65 ± 0.03	3.13 ± 0.01
Valerophenone	1.94 ± 0.03	2.04 ± 0.01	2.41 ± 0.01	2.63 ± 0.05	3.17 ± 0.01
Isovalerophenone	1.86 ± 0.01	1.95 ± 0.01	2.26 ± 0.01	2.49 ± 0.02	2.91 ± 0.01
Hexaphenone	1.86 ± 0.01	1.98 ± 0.01	2.30 ± 0.02	2.50 ± 0.03	3.01 ± 0.03
Heptaphenone	1.81 ± 0.01	1.94 ± 0.01	2.25 ± 0.03	2.43 ± 0.01	2.87 ± 0.03
Octaphenone	1.77 ± 0.01	1.89 ± 0.01	2.18 ± 0.01	2.36 ± 0.02	2.74 ± 0.03
Nonaphenone	1.71 ± 0.03	1.81 ± 0.01	2.11 ± 0.03	2.29 ± 0.02	2.61 ± 0.01
Decaphenone	1.69 ± 0.02	1.77 ± 0.01	2.06 ± 0.01	2.12 ± 0.01	2.57 ± 0.01
Myristophenone	1.64 ± 0.05	1.69 ± 0.01	1.98 ± 0.02	2.06 ± 0.01	2.47 ± 0.01

[a] A diffusion coefficient at 90°C was also obtained for this compound; D_{AB} = 3.80 ± 0.03.

good, the largest deviation being about 3%. These results attest to the reproducibility of the method.

Table II shows the diffusion coefficients of 12 phenones in heptane at five temperatures. Also indicated in Table II are the standard deviations associated with the measurements. At worst, the precision (in percent relative standard deviation) is about 2-3% but in most instances it is less than 1%.

The general formula of the straight chain phenones used in this study is



As shown in Table II two branched phenones were also included.

As expected, the diffusion coefficients decrease with an increase in the length of the alkane chain of the phenone. Moreover, the two branched phenones diffuse slower than their straight chain isomers. This is in accord with our previous findings.[18]

Attempts were made by several workers to take into account the size of the molecules by estimating the end-to-end length of the molecules or related parameters. Thus, Couper and Stepto[30] used the root mean square distance of a chain element from the molecular center of mass. Burkhart and Merrill[31] have calculated the frictional coefficients by adding the contribution of the average distance between two segments in the chain. Jain and Tewari,[32] apparently not being aware of the study by Burkhart and Merrill,[31] used the same approach as the latter authors. These studies are essentially modifications of the Kirkwood-Riseman[33] treatment where the friction coefficients once calculated, are utilized in the Einstein equation.

The effect of the molecular size on the diffusion has been scantly studied experimentally. Nir and Stein[25] indicate that a plot of log D_{AB} vs. log M, where M is molecular weight of the diffusant, for large molecular weight is a straight line with a slope of $-\frac{1}{3}$. That relationship fails, however, when the diffusant is roughly of the same dimension as the solvent. Couper and Stepto[30] indicate that a plot of log D_{AB} vs. the log of some linear function of the molecular weight is a straight line with a slope of $-\frac{1}{2}$. Table III shows least-squares fit data of such plots for the straight phenones of this study. The theoretical slope of log D_{AB} vs. log M should be about $-\frac{1}{2}$ (ref 25, 30, 33) depending on the size of the diffusant. From Table III, it is seen that the slope may be a function of the temperature.

Figure 2 shows a plot of D_{AB} vs. the carbon number of the straight chain phenones. For the sake of pictorial clarity, data at only two temperatures are shown. Also given in the figure are the diffusion coefficients of some alkanes in benzene which were taken from the work of Burkhart and Merrill.[31] The relationship is obviously not linear. Recently, Lo[26] found a linear relationship between D_{AB} and the log of the carbon number. We have tried such a plot and indeed over a short range of carbon numbers the plot is linear. However, when the plot encompasses many compounds in the homologous family, the linearity is not maintained. Indeed there is no reason to expect a direct relationship. As more methylene groups are added to the molecule, the larger are the number of conformations that molecular segments can have. Thus as the molecule gets larger, the addition of a CH_2 group does not affect greatly the overall shape of the solute, and this is reflected in the smaller decrease in D_{AB} at large carbon numbers. Qualitatively this agrees with the treatment of Vadovic and Colver[34]

Table III. Data for Straight Line Fits of ln D_{AB} vs. ln M for Straight Chain Phenones

Temp, °C	Slope	Intercept	Correlation coefficient
40	−0.401	−8.79	0.976
50	−0.483	−8.31	0.967
60	−0.487	−8.13	0.975
70	−0.570	−7.62	0.970
80	−0.568	−7.46	0.977

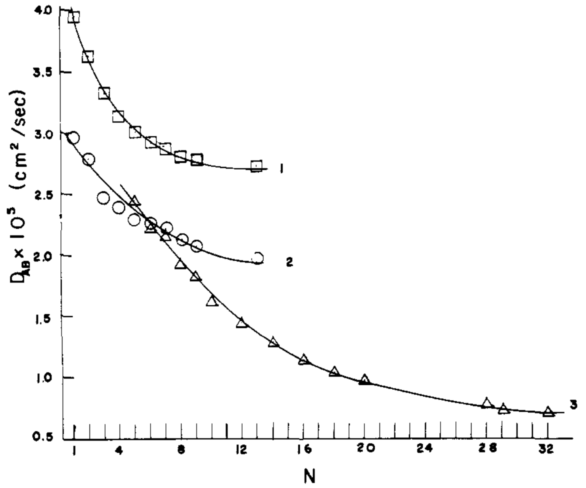


Figure 2. Diffusion coefficient vs. carbon number; Phenones at: (1) 80°C, (2) 60°C, (3) $CH_3(CH_2)_{N-2}CH_3$ at 25°C in benzene.[31]

$$\frac{D_{AB}\eta_B M_B}{\rho_B T} = (0.219 \times 10^{-6}) \times \left(\frac{V_{mB}}{V_{mA}}\right)^{2/3}\left(\frac{M_A + M_B}{2M_A}\right)^{1/2} V_{mB}^{2/3} \quad (4)$$

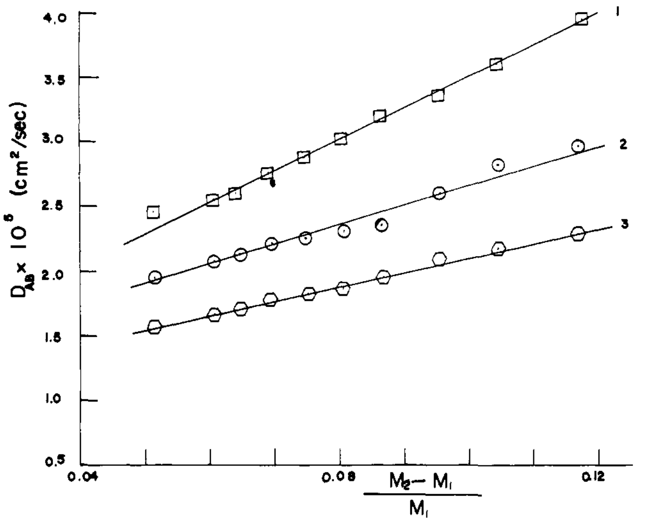


Figure 3. Diffusion coefficient vs. incremental molecular weight increase: (1) 80°C, (2) 60°C, (3) 40°C.

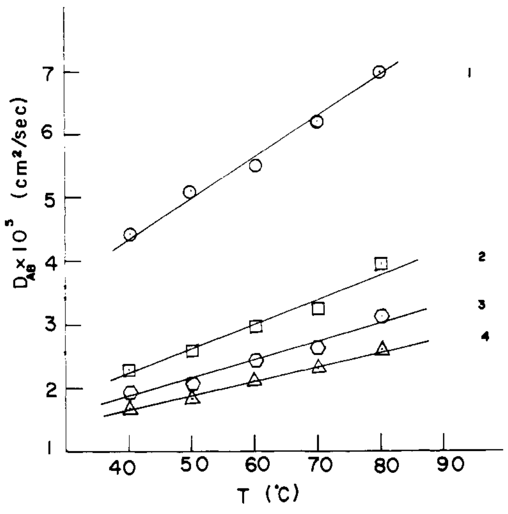


Figure 4. D_{AB} vs. T (°C): (1) benzene, (2) acetophenone, (3) valerophenone, (4) nonaphenone.

Table IV. Data for the Straight Line Fit of D_{AB} vs. $(M_2 - M_1)/M_1$

Temp, °C	Slope $\times 10^4$	Intercept $\times 10^5$	Correlation coefficient
40	1.02	1.08	0.993
50	1.33	0.953	0.983
60	1.56	1.12	0.992
70	1.98	0.975	0.983
80	2.33	1.17	0.992
25[a]	0.904	0.529	0.977

[a] From the diffusion of hydrocarbons in benzene in ref 31.

Table V. B' and m values for the Phenones

Compound	m	$10^4 B'$ (cm²/s)	Correlation coefficients[a]
Acetophenone	1.64	4.29	0.998
Propiophenone	1.60	3.73	0.994
n-Butyrophenone	1.28	2.01	0.973
Isobutyrophenone	1.33	2.11	0.975
Valerophenone	1.48	2.66	0.980
Isovalerophenone	1.37	2.04	0.984
Hexaphenone	1.43	2.35	0.983
Heptaphenone	1.38	2.08	0.988
Octaphenone	1.32	1.83	0.989
Nonaphenone	1.30	1.71	0.990
Decaphenone	1.22	1.47	0.967
Myristophenone	1.22	1.41	0.967
Benzene	1.36	5.07	0.998

[a] The correlation coefficients are for the plot of $\ln D$ vs. $\ln((\rho_0 - \rho)/\rho)$.

M is molecular weight, η viscosity, ρ density, V_m molar volume at melting point, and subscripts A and B indicates solute and solvent. The molecular weight term shows that as M_A increases, the whole terms can approach an asymptote. In addition, the change in the molar volume term is not as important as the molecular weight term. Examination of the data in Table 2 of ref 34 also shows a nonlinear dependence on the carbon number.

The functionality of the diffusion coefficients on the molecular weight is perhaps related to an *incremental* increase in that weight. More desirable, perhaps, would have been a relationship of some volume function, calculated using the procedure outlined in references 30, 31, and 32. With the phenones, however, such calculations may not be simple due to the presence of the benzene ring and a ketone group. It was felt, however, that the molecular weights could be representative of the volume (although it is recognized that this can be a serious assumption). Figure 3 shows a plot of D_{AB} vs. the increment in the molecular weight divided by the molecular weight of the lighter component for the ten linear phenones. For clarity, plots at only three temperatures are shown. $M_2 - M_1$ is the molecular weight of a CH_2 group. The straight lines were least-squares fitted and they show excellent correlation. Table IV shows the slopes, intercepts, and correlation coefficients for all data gathered here and for some of the data from Burkhart and Merrill.[31] The high correlation coefficients indicate very good linear functionality between the plotted parameters. Examination of Table IV indicates that for the phenones the slopes of the lines increase with increasing temperature while the intercepts are roughly constant, $(1.06 \pm 0.09) \times 10^{-5}$. The increase in the slope with T is reasonable since at the higher diffusion coefficient it is to be expected that increasing the molecular weight will have a greater effect. Table IV and Figure 3 also indicate that the effect of adding a CH_2 group to the molecule is greatest when the overall size is small. A word of caution must be given here. The intercept occurs at $M_1 \rightarrow \infty$. At very high M_1 values, the straight line behavior most likely will not be obeyed. However, over the range of molecular weight normally encountered in realistic cases the straight line seems to hold. The validity of such plots should be investigated further in different solute-solvent systems.

The temperature dependence of the diffusion coefficients is of practical importance. As indicated before the rigorous hard core theories indicate that in order to understand temperature effect the density of the mixture must be kept constant. Under this condition Chandler[10] indicates that the diameter of the hard sphere will decrease with increasing temperature. Since the present study was carried out at a constant pressure, the density varied from 0.6663 g/cm³ at 40°C to 0.6309 g/cm³ at 80°C, a change which is quite significant and which prohibits exact hard sphere calculation. However, the data can be utilized to examine such empirical relationships as suggested by Hildebrand.[6] This is particularly important since some workers, such as Cullinan and Kosanovich,[23] are beginning to use the fluidity approach for predictive purposes.

Following the discussion of Ertl and Dullien,[8] and assuming that in dilute solutions the volume of the pure solvent is the important quantity,[23] eq 2 can be written in terms of the density of heptane

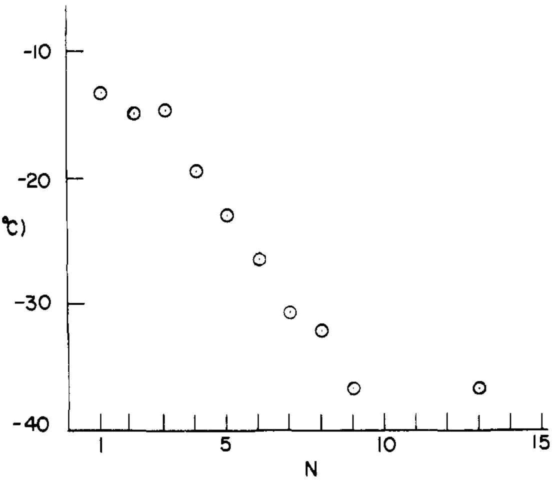


Figure 5. T_0 vs. carbon number.

Table VI. Data for the Straight Line of D vs. T°C

Compound	Slope $\times 10^{-7}$	Intercept $\times 10^{-6}$	Correlation coefficient	T_0 (D = 0), °C
Acetophenone	4.12	5.54	0.994	−13.4
Propiophenone	3.76	5.66	0.990	−15.0
n-Butyrophenone	3.48	5.05	0.971	−14.5
Isobutyrophenone	2.78	7.88	0.971	−28.3
Valerophenone	3.05	6.08	0.974	−19.9
Isovalerophenone	2.64	7.10	0.980	−26.9
Hexaphenone	2.82	6.36	0.976	−22.8
Heptaphenone	2.61	6.94	0.982	−26.6
Octaphenone	2.41	7.42	0.986	−30.8
Nonaphenone	2.28	7.38	0.988	−32.4
Decaphenone	2.10	7.80	0.960	−37.1
Myristophenone	2.03	7.50	0.962	−36.9
Benzene	6.36	18.5	0.996	−29.0

$$D_{AB} = B' \left(\frac{\rho_0 - \rho}{\rho} \right)^m \tag{5}$$

Table V shows the values of B' and m for the phenones and benzene. The exponent m was obtained by least-squares fitting a straight line to a ln D vs. ln $((\rho_0 - \rho)/\rho)$ plot.

Hildebrand and Lamoreaux[7] showed that plots of D vs. T gave straight lines. Figure 4 shows plots of D_{AB} vs. T for several phenones to which straight lines were fitted. The complete set of data, i.e., the slope, intercept, and correlation coefficients is shown in Table VI. It is of interest to note that the correlation coefficients are roughly the same as those in Table V. Least-squares fit of D to a polynomial in T did not improve much the correlation coefficients. For that reason, we chose to fit straight lines to the data. The trend in the slope is to be noted; as the chain length increases, the magnitude of the slope decreases.

According to Hildebrand,[6,7] an extrapolation of plots such as those in Figure 4 to zero diffusion coefficient, i.e., zero fluidity, should converge to a single temperature value. This was not found to be the case in this study. The last column in Table VI, which shows the extrapolated temperature T_0 at which D_{AB} = 0, indicates that as the molecular weight increases, T_0 decreases. Graphically this is shown in Figure 5 when T_0 is plotted vs. the carbon number, N, of the phenones' side chain. The data in Figure 5 were least-squares fitted to several functions and the best fit was obtained with a second-order polynomial. From a physical point of view this does not seem to be meaningful and at this point the exact relationship between T_0 and N is unknown to us. It is possible that as N increases, the value of T_0 will approach an asymptote. A tentative explanation might lie in the fact that as the phenone molecule increases with relation to the solvent, the latter "senses" only segmental motion of the solute, as described by Van Geet and Adamson.[35]

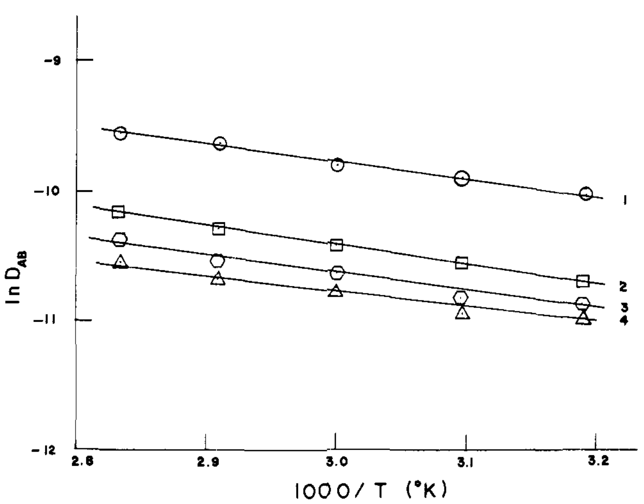


Figure 6. ln D_{AB} vs. 1000/T (°K); (1) benzene, (2) acetophenone, (3) valerophenone, (4) nonaphenone.

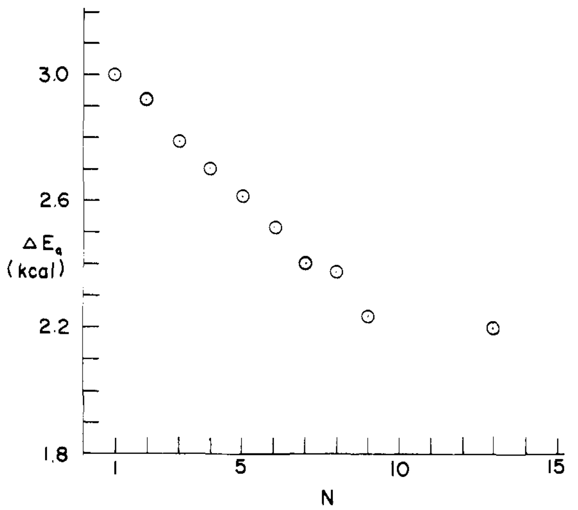


Figure 7. "Activation" energy (kcal) vs. carbon number.

Table VII. "Activation" Energy Data for Compounds in This Study

Compound	ΔE (kcal)	Correlation Coefficient
Acetophenone	3.00	0.998
Propiophenone	2.92	0.994
n-Butyrophenone	2.79	0.976
Isobutyrophenone	2.43	0.974
Valerophenone	2.70	0.980
Isovalerophenone	2.49	0.983
Hexaphenone	2.61	0.982
Heptaphenone	2.51	0.987
Octaphenone	2.40	0.989
Nonaphenone	2.37	0.989
Decaphenone	2.23	0.966
Myristophenone	2.22	0.966
Benzene	2.48	0.998

Figure 6 shows plots of ln D_{AB} vs. 1000/T for several of the phenones and for benzene. Ertl and Dullien[8] indicated that at temperatures well above the freezing point, the Arrhenius type plot can be quite suitable without implying an activation model. Table VII shows the so-called "activation" energies, ΔE, and the correlation coefficients of the least-squares fitted straight lines for each of the solutes. The correlation coefficients indicate a fairly good linear relationship between ln D_{AB} and $1/T$. Examination of the ΔE values shows that, for the straight chain phenones, the "activation" energy decreases as the chain length increases. This can conceivably yield the contribution of a CH_2 group to the "activation" energy. Figure 7 shows a plot of ΔE vs. the carbon number of the alkane side chain. The general features of Figure 7 are very similar to those shown in Figure 5, and the discussion made regarding the latter figure might hold true here. To the advocate of the rate approach, the data in Table VII and Figure 7 indicate that on the average, each CH_2 group contributes initially about 73 cal to the "activation" energy, and that the contribution decreases as N increases. Ertl and Dullien[36] reported a linear relationship between "activation" energy and the log of the carbon number in the case of self-diffusion of some liquids, provided the carbon number is large enough. Such was not the case in the present study.

The similarities between Figures 5 and 7 are noteworthy. Although at this point we cannot offer any explanations, we feel that the resemblance is more than a coincidence. At this point, additional data are needed, especially at low temperatures where the fluidity approach should deviate from the picture given here. In addition, to take full advantage of the more rigorous hard sphere theories, data at a given temperature but at varying pressures should be gathered. This will help in adjusting the model for large nonspherical molecules diffusing in mixtures.

References and Notes

(1) A. Einstein, "Investigation on the Theory of the Brownian Movement", Dover Publication, New York, N.Y., 1956.
(2) S. Glasstone, K. J. Laidler, and H. E. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, N.Y., 1941.
(3) S. A. Rice and J. G. Kirkwood, *J. Chem. Phys.*, **31**, 901 (1954).
(4) R. K. Ghai, H. Ertl, and F. A. L. Dullien, *AIChE J.* **19**, 881 (1973); **20**, 1 (1974).
(5) A. J. Batschinski, *Z. Phys. Chem.* (*Leipzig*), **84**, 643 (1913).
(6) J. H. Hildebrand, *Science*, **174**, 490 (1971).
(7) J. H. Hildebrand and R. H. Lamoreaux, *Proc. Nat. Acad. Sci. U.S.A.*, **71**, 3321 (1974).
(8) H. Ertl and F. A. L. Dullien, *J. Phys. Chem.*, **77**, 3007 (1973).
(9) B. J. Alder, W. E. Alley, and J. H. Dymond, *J. Chem. Phys.*, **61**, 1415 (1974).
(10) D. Chandler, *J. Chem. Phys.*, **62**, 1358 (1975).
(11) J. H. Dymond, *J. Chem. Phys.*, **60**, 969 (1974).
(12) J. DeZwaan and J. Jonas, *J. Chem. Phys.*, **62**, 4036 (1975).
(13) R. B. Bird, W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena", Wiley, New York, N.Y., 1960.
(14) G. I. Taylor, *Proc. R. Soc. London, Ser. A*, **219**, 186 (1953).
(15) G. I. Taylor, *Proc. R. Soc. London, Ser. A*, **225**, 473 (1954).
(16) A. C. Ouano, *Ind. Eng. Chem. Fundam.*, **11**, 268 (1972).
(17) K. C. Pratt and W. A. Wakeham, *Proc. R. Soc. London, Ser. A*, **336**, 393 (1974).
(18) E. Grushka and E. J. Kikta, Jr., *J. Phys. Chem.*, **78**, 2297 (1974).
(19) H. Komiyama and J. M. Smith, *J. Chem. Eng. Data*, **19**, 384 (1974).
(20) P. F. Jhaveri, R. N. Trivedi, and K. Vasudera, *Diffus. Solutes Solution Fiber Syst., Proc. Symp.* (1973); *Chem. Abstr.*, **81**, 68883 (1974).
(21) A. C. Ouano and J. A. Carothers, *J. Phys. Chem.*, submitted for publication.
(22) B. J. Alder and J. H. Hildebrand, *Ind. Eng. Chem., Fundam.*, **12**, 387 (1973).
(23) H. T. Cullinan, Jr., and G. Kosanovich, *AIChE J.*, **21**, 195 (1975).
(24) J. C. Shieh and P. A. Lyons, *J. Phys. Chem.*, **73**, 3258 (1969).
(25) S. Nir and W. A. Stein, *J. Chem. Phys.*, **55**, 1598 (1971).
(26) H. Y. Lo, *J. Chem. Eng. Data*, **19**, 236 (1974).
(27) S. A. Sanni, C. J. D. Fell, and P. Hutchison, *J. Chem. Eng. Data*, **16**, 424 (1971).
(28) W. F. Calus and M. T. Tyn, *J. Chem. Eng. Data*, **18**, 377 (1973).
(29) L. R. Wilke and P. Chang, *AIChE J.*, **1**, 264 (1955).
(30) A. Couper and R. F. T. Stepto, *Trans. Faraday. Soc.*, **65**, 2486 (1969).
(31) R. D. Burkhart and J. C. Merrill, *J. Chem. Phys.*, **46**, 4985 (1967).
(32) D. V. S. Jain and K. K. Tewari, *Chem. Phys. Lett.*, **10**, 487 (1971).
(33) J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16**, 1565 (1948).
(34) C. J. Vadovic and C. P. Colver, *AIChE J.*, **19**, 546 (1973).
(35) A. L. Van Geet and A. W. Adamson, *J. Phys. Chem.*, **68**, 238 (1964).
(36) H. Ertl and F. A. L. Dullien, *AIChE J.*, **19**, 1215 (1973).

All-Electron Nonempirical Calculations of Potential Surfaces. III. Dissociation of Ketene into CH_2 and CO

Phil Pendergast and William H. Fink*

Contribution from the Department of Chemistry, University of California, Davis, California 95616.

Received February 13, 1975

Abstract: Ab initio calculations on the lower lying states of ketene have been performed using excited-state SCF and CI methods. The ground-state and first excited-state surfaces were searched so as to nearly find the optimum theoretical molecular geometry. Dissociations along both linear and bent paths departing from these geometries were then examined. The excited-state assignments of ketene and its controversial photochemistry are discussed in light of the calculated molecular orbital correlation diagrams, the SCF energies, the configuration interaction energies, and the weights of the configurations.

A qualitative and semiquantitative understanding of photochemical processes should be possible by quantum chemical calculations of the potential-energy surfaces involved in these processes. The present work is a state of the art application of quantum chemical methods to the primary photochemical decomposition reactions of ketene ($H_2C{=}C{=}O$). While the reliability of SCF methods of calculation for closed-shell, ground-state molecules in the vicinity of the equilibrium internuclear geometry is reasonably well understood, the situation is less clear for open-shell, excited-state molecules or for geometries far from the ground-state equilibrium. In certain situations, the inadequacy of the valence-shell atomic orbitals to describe low-lying Rydberg levels has become apparent;[1] in other situations, the states are simply not adequately described by a single-determinant wave function;[2] this latter difficulty often becomes particularly acute at asymptotic values of intermolecular distances where the imposition of a particular occupation precludes the SCF wave function from dissociating to the correct molecular or atomic fragments. The present work includes both an extended basis set and limited configuration interaction calculation in order to be reasonably sure of avoiding these possible deficiencies of a valence-shell SCF calculation. There remains considerable controversy over

---

*Author to whom correspondence should be addressed.