(19) P. Pulay, *Mol. Phys.*, **21**, 329 (1971); G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Amer. Chem. Soc.*, **89**, 3396 (1967); J. L. Duncan and I. M. Mills, *Spectrochim. Acta*, **20**, 523 (1964); J. L. Duncan, *ibid.*, **20**, 1197 (1964); T. Shimanouchi, *Pure Appl. Chem.*, **7**, 131 (1963); M. Pariseau, E. Wu, and J. Overend, *J. Chem. Phys.*, **39**, 217 (1963); C. W. F. T. Pistorius, *ibid.*, **27**, 965 (1957).

(20) Because of the sizable amount of structural and thermodynamic data available for hydrocarbons, extensive verification of hydrocarbon parameters has been possible. A multitude of diverse compounds has been studied under several force fields by Schleyer and coworkers.[21] That the results display not only consistency with experiment, but consistency among the different force fields as well, is justification for confidence in the empirical force-field approach when applied to compounds containing only hydrogen and carbon.

(21) E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 8005 (1973).

(22) These conventions do not follow the definitions of flipping and nonflipping rings given in ref 4a, in which ring orientations are described with respect to the reference plane. The definitions used here were chosen for programming considerations.

(23) Calculations were performed on an IBM 360/91 computer using double precision arithmetic. Analysis was aided by viewing all structures in three dimensions using the facilities of the Princeton Computer Graphics Laboratory (E & S LDS-1/DEC PDP-10), supported in part by a grant from the National Institutes of Health.

(24) Y. Sasaki, K. Kimura, and M. Kubo, *J. Chem. Phys.*, **31**, 477 (1959).

(25) D. M. Hawley and G. Ferguson, *J. Chem. Soc. A*, 2059 (1968).

(26) The equilibrium position, or energy minimum, of the harmonic potential used to approximate bond stretching forces. See ref 4f.

(27) Results for r_0(C–Mes) = 1.50 Å are those calculated for 1 in ref 4f.

(28) Experimental data in Figure 1 are taken from the following sources: (a) bond lengths, r(Z–C): Z = CH, ref 30; Z = B, ref 4c; Z = P, for triphenylphosphine, ref 33; Z = SiH, for tetraphenylsilane, M. Yokoi, *Bull. Chem. Soc. Jap.*, **30**, 100 (1957); Z = GeH, for tetraphenylgermane, A. Karipides and D. A. Haller, *Acta Crystallogr. Sect. B*, **28**, 2889 (1972); Z = As, for tri-*p*-tolylarsine, J. Trotter, *Can. J. Chem.*, **41**, 14 (1963). (b) Activation energies: Z = CH, ref 4e; Z = B, for bis(2,6-xylyl)-1-(3-isopropyl-2,4,6-trimethylphenyl)borane, ref 4i; Z = P, As, ref 7. Since ΔG^* values reported in ref 7 are not those for the two-ring flip (see footnote 20 in ref 4e), ΔG^* values reported here are appropriately corrected as previously described.[4e] Z = SiH, ref 4d; Z = GeH, R. J. Boettcher, unpublished results.

(29) P. Andersen, *Acta Chem. Scand.*, **19**, 622 (1965).

(30) (a) J. F. Blount and K. Mislow, *Tetrahedron Lett.*, in press; (b) J. F. Blount, C. A. Maryanoff, and K. Mislow, *ibid.*, in press.

(31) J. P. Hummel, unpublished results.

(32) D. R. Lide, Jr., *J. Chem. Phys.*, **19**, 1605 (1951).

(33) J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

(34) It had earlier been concluded,[35a] on the basis of the essential identity of the dipole moments of triphenylphosphine and **4**, that the C–P–C bond angles in the latter should not be appreciably larger than those in the former,[33] *i.e.*, that they should assume a value near 103°. Evidently the rehybridization accompanying expansion of the C–P–C bond angles from 103 to 108–111° produces compensatory changes in the dipole moment, as discussed elsewhere.[35b]

(35) (a) E. J. Halpern and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 5224 (1967). (b) M. P. Warchol, E. N. DiCarlo, C. A. Maryanoff, and K. Mislow, *Tetrahedron Lett.*, in press.

Special Effect of Pressure on Highly Hindered Reactions as a Possible Manifestation of the Hammond Postulate[1]

W. J. le Noble† and T. Asano

Contribution from the Department of Chemistry, State University of New York, Stony Brook, New York 11794.

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Abstract: In this paper, we attempt to reach an understanding of the phenomenon that among those reactions which are promoted by the application of hydrostatic pressure, the most highly hindered ones tend to be accelerated most. The example discussed here is the Menshutkin reaction of methyl, ethyl, and isopropyl iodide with pyridine and with 2,6-dimethyl-, -ethyl-, isopropyl- and -*tert*-butylpyridine; the known activation volumes for these reactions in acetone steadily become more negative as the interfering groups are made larger. We now report the partial molal volumes of the free bases and the alkylating agents in acetone and methanol and of the *N*-methylpyridinium iodides in methanol. The data do not support the Gonikberg theory, according to which the progressive shrinking of the transition state with increased hindrance is due to "interpenetration" of the interfering groups. Instead, the observations can be accounted for by the Hammond postulate, according to which the transition states in the more hindered reactions should be more "product-like". We also report an anomalously large volume increase from 2,6-diisopropyl- to -*tert*-butylpyridine in methanol and conclude that hydrogen bonding to the latter base is extremely weak or absent altogether.

Among chemists interested in the effects of pressure on the rate constants of reactions in solution,[2] it is a well-known fact that pressure induced accelerations are generally greatest for sterically hindered reactions. These accelerations are related to the activation volume by the expression

$$-\partial \ln k/\partial p = \Delta V^*/RT$$

ΔV^* is therefore negative in a reaction promoted by pressure,[3] the more so the greater the acceleration. Some extreme examples have been noted; in fact, Okamoto has encountered sterically hindered reactions under pressure which are apparently not detectable at 1 atm at all.[4] This generalization—the greater the hindrance, the greater the acceleration—is of obvious interest in that it may have synthetic applications, and hence in several high pressure laboratories further examples have been sought and discovered. Most of these instances have centered around the Menshutkin reaction; most recently, a report from our laboratory[5] listed the systematic increase in the pressure-induced rate accelerations as the number of carbon atoms is increased in the reaction of methyl, ethyl, and isopropyl iodide with pyridine and 2,6-dimethyl-, -ethyl-, -isopropyl-, and -*tert*-butylpyridine. The observations in this report may be summarized by the statement that $\Delta V_0^{\ddagger}$ becomes more negative by about 2 cm^3/mol for each additional methylene group near the reaction site.

To date, only the late Gonikberg and his coworkers have ventured an explanation of this phenomenon.[6] They assume that the length of the newly forming C–N bond is equal in the transition states of all these reactions (and 10% longer than the normal equilibrium value), and that no distortions occur except in the flattening methyl group, and they propose that the increasingly negative activation volume is due to "overlapping volumes", i.e., to increased "interpenetration" of the interfering groups. This proposal was supported by calculations showing that these assumptions can produce remarkably good agreement with experiment.[7] This agreement must be largely fortuitous, however. First of all, the assumption of a bond length in the transition state only 10%

longer than normal is almost surely an underestimate; 20–50% seems to be the range of estimates for a wide variety of transition states.[8] Menshutkin reactions in particular are believed to have "early" transition states, i.e., to have long C–N bonds in the activated complex.[9] Secondly, as Hamann and Weale have pointed out, this treatment completely ignores the effect of solvation; yet the very large "electrostriction" due to solvation is clearly indicated by the fact that the activation volumes for Menshutkin reactions (-20 to -50 cm^3/mol) are usually several times larger than those for any other types of displacement reaction (-5 to -15 cm^3/mol^1).[2,10] The errors due to those two assumptions (an underestimated C–N bond length and neglected solvation) tend to cancel. Furthermore, the assumption of molecules undistorted in the face of such crowding seems unrealistic; thus, the highly successful Westheimer treatment of steric interactions[11] is based on accommodation by bond bending. Indeed, the idea of interpenetrable groups runs counter to the whole history of the interpretation of steric effects with its emphasis on hard atoms, extremely sharp increases of repulsions with shortening distances (exemplified by the Lennard-Jones potential), and so on. A related point is that there are no known examples of interpenetration in molecules of isolable substances. Although minor increases in density are usually observed when hindered isomers are compared with uncrowded ones (for instance, ortho with meta or para isomers), there are no instances of really substantial differences in the molar volumes of isomers; this very fact has enabled chemists to make use of the concept of parachor.

An alternative possibility, not yet offered elsewhere so far as we know, is that the phenomenon is a consequence (or perhaps better, a demonstration) of the Hammond postulate. According to this postulate, when two similar reactions differ greatly in the amount of energy released, the more exothermic one will be faster and have an earlier transition state (see Figure 1).[9] Since the reaction coordinate is ultimately defined by the nuclear positions, the partial molar volume of the reacting solute is more closely related to the reaction coordinate than any other variable amenable to laboratory measurement. We therefore decided to test our hypothesis (to wit, that the special pressure-induced acceleration of hindered reactions is a manifestation of the Hammond postulate) by measuring the partial molar volumes of both reactants and products in several reactions differing greatly in their rates only because of steric hindrance. The argument is graphically demonstrated by means of Figure 2.

In this illustration, we have drawn straight lines between initial and final volumes vs. the reaction coordinates; this of course may prejudice the case somewhat. The true relations are virtually unknowable, but we may point out that the least motion principle,[12] although discredited for more complex bond reorganizations[13] in favor of the Woodward–Hoffmann rules,[14] is almost certainly valid for such simple bond formations as occur in Menshutkin reactions. Now if "interpenetration" is alone responsible for the steric pressure effect, the volume decreases observed earlier in the transition states should have become even more pronounced when the molecules have arrived in their final states; if the Hammond postulate accounts for this difference, then there is no reason to suppose that the partial volumes of the final products are in any way abnormal.

Experimentally, the following approach is therefore indicated. One simply measures the reaction volumes and compares them with the activation volumes. If the Gonikberg theory is correct, the latter should be a constant fraction of the former; if the Hammond postulate is operating, this fraction should increase as the hindrance increases. In the event, we ran into some experimental difficulties that made it impossible to study the complete series; thus, synthetic problems limited us to the 2,6-dialkyl-*N*-methylpyridinium salts. A second problem forces us to compare the activation volume in one solvent (acetone) with the reaction volumes in another (methanol). The reason for this is that the more hindered reactions are so slow that solvolysis of the alkyl iodides becomes a significant side reaction; on the other hand, ion pairing, and perhaps even further aggregation, makes it impossible to measure the partial molal volumes of the product salts in acetone with any kind of precision. While there may be solvents in which both solvolysis and ion association can be prevented (for instance, hexamethylphosphoramide), these solvents generally have high freezing points, and this precludes their use as high-pressure media. We do not believe that this drawback is very serious. Thus, with one minor exception noted below, there are no very large differences in partial molal volume of the pyridines when acetone and methanol are compared. Likewise, while the activation volumes ($\Delta V^{\ddagger}$) are somewhat solvent dependent, the differences between them ($\Delta\Delta V^{\ddagger}$) are not; the trend is the same.

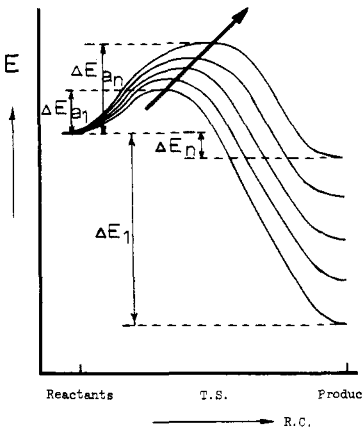

Figure 1. The Hammond postulate: a rapid reaction with "reactant-like" transition state vs. a slower reaction with "product-like" activated complex.

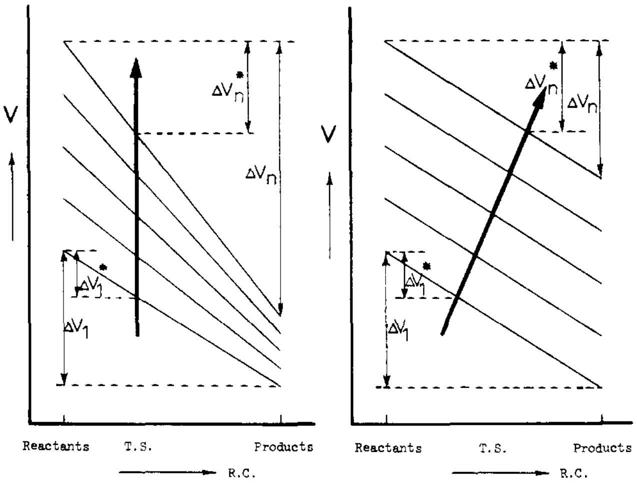

Figure 2. The partial molar volume of a reacting species: (a) if "interpenetration" of groups accounts for the differences in activation volume observed when hindered reactions are compared with unhindered ones; (b) if the Hammond postulate is responsible.

Partial molal volumes can be measured by injecting various small known quantities of concentrated solutions into a suitable dilatometer[15] or by means of density determinations, which can be carried out with great precision by the magnetic float[16] or differential balance[17] techniques. Unfortunately, the outstanding sensitivity possible with these methods is of no avail to us since at such low concentrations, ionization of the free bases becomes appreciable in methanol. Attempts to circumvent this problem by the use of dilute solutions of strong bases lead to other problems, and hence we settled for the pycnometric technique,[18] which still has a sensitivity of about 5×10^{-6} g/ml and can be used down to concentrations of about 0.02 mol/l. The equilibrium constants for ionic association of chlorides in methanol generally appear to be well below 10 so that the errors due to this phenomenon in the concentration range used in our work are small.[19]

The apparent molar volume ϕ_V of a solute is almost always concentration dependent, and hence extrapolation is required to calculate the partial molar volume at infinite dilution $\phi_V{}^0$. ϕ_V is given by

$$\phi_V = \frac{M}{d_0} - \left(\frac{d - d_0}{d_0}\right)\frac{1000}{C}$$

where M is the molecular weight of the solute, d and d_0 are the densities of the solution and of the solvent, respectively, and C is the molarity.[20] In the case of the free bases, a simple plot of ϕ_V vs. C, extrapolated to zero concentration, gives the partial molar volume. For the hydrochlorides, the Rodrich-Rosenfeld equation is preferred[21] when methanol solutions are used:

$$\phi_V = \phi_V{}^0 + S_V C^{1/2} + b_V C$$

where S_V for methanol has the theoretical value of 15.77.[22] Figure 3 summarizes our observations; the limiting values of ϕ_V are shown in Table I.

The data in Table I and those of ref 5 can be now drawn together; the results are shown in Table II. The result clearly shows that by the volume criterion, the transition state becomes more product-like as the reaction becomes more hindered. The data involving the *tert*-butyl substituent involve the largest uncertainty. Since this reaction simply does not occur at atmospheric pressure, $\Delta V_0{}^{\ddagger}$ in this case is based on data obtained at 4 kbars and more; it seemed possible at the time that the absolute value had in fact still been underestimated. As far as the $\Delta\phi_V{}^0$ value is concerned, that value is based on an extrapolation of the data above it in the same column in Table II. Since no extreme discontinuities were found at *tert*-butyl in any of the series of partial volume measurements including the hydrochlorides,[23] we are confident that $\Delta\phi_V{}^0$ for the formation of this salt lies between −50 and −60 cm^3/mol. Thus, it is reasonable to conclude that the transition state strongly resembles the product.[24]

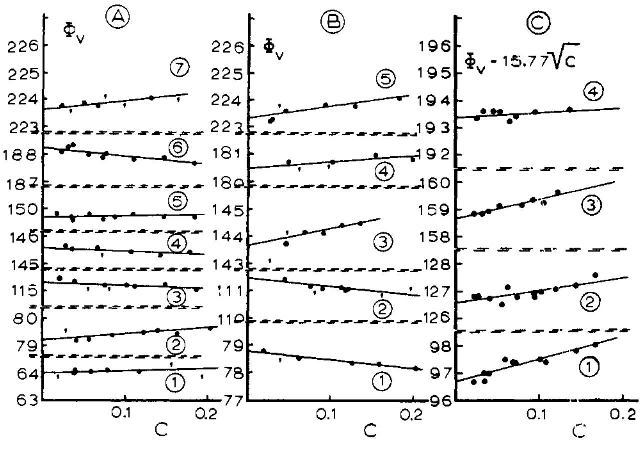

Figure 3. Results of measurements showing approach of the molar volumes to their limiting values. (A) In acetone at 25.00°; 1, methyl iodide; 2; pyridine; 3, 2,6-lutidine; 4, 2,3,5,6-parvoline; 5, 6, and 7, 2,6-diethyl-, isopropyl-, and -*tert*-butylpyridine, respectively. (B) In methanol at 25.00°; 1, pyridine; 2, 2,6-lutidine; 3, 4, and 5, 2,6-diethyl-, -isopropyl-, and -*tert*-butylpyridine, respectively. (C) In methanol at 25.00°: 1-4, *N*-methylpyridinium iodide, 2,6,*N*-trimethylpyridinium iodide, and 2,6-diethyl- and -isopropyl-*N*-methylpyridinium iodide, respectively.

Table I. Partial Molar Volumes[a] of Several Pyridines and Their *N*-Methyl Iodides in Infinite Dilution at 25°

2,6-Substituents	Free base in acetone[b]	Free base in methanol	*N*-Methyl iodide in methanol
H	79.21 ± 0.23	78.82 ± 0.24	96.69 ± 0.23
Me	115.30 ± 0.18	111.12 ± 0.66	126.56 ± 0.27
Et	149.70 ± 0.14	143.67 ± 0.45	158.65 ± 0.20
i-Pr	188.24 ± 0.19	180.47 ± 0.38	193.39 ± 0.31
t-Bu	223.67 ± 0.27	223.31 ± 0.51	

[a] In cm^3; the errors stated make the data given reliable to within the 95% confidence limits. [b] For methyl, ethyl, and isopropyl iodide, $\bar{V}_0$ was found to be 64.00 ± 0.25, 83.64 ± 0.27, and 103.50 ± 0.43 cm^3/mol, respectively; parvoline (2,3,5,6-tetramethylpyridine) has a $\bar{V}_0$ of 145.60 ± 0.22 cm^3/mol.

Table II. Activation and Reaction Volumes of the Reaction of Methyl Iodide with 2,6-Disubstituted Pyridines

2,6-Substituents	$\Delta V_0{}^{\ddagger}$, cm^3/mol[a]	$\Delta\phi_V{}^0$, cm^3/mol[b]	$\Delta V_0{}^{\ddagger}/\Delta\phi_V{}^0$
H	−21.9	−46.1	0.47
Me	−24.4	−48.5	0.50
Et	−27.3	−49.0	0.55
i-Pr	−30.2	−51.0	0.59
t-Bu	<−50	−50 to −60[c]	~0.90

[a] Reference 5. [b] $\phi_V{}^0$ (*N*-Me pyr$^+$ I$^-$) − $\phi_V{}^0$ (pyr) − $\phi_V{}^0$ (Me I). [c] By extrapolation.

We also made an attempt to determine some of the reaction volumes in acetone directly by means of dilatometric measurements. While the precision is poor, two observations are clear: the contractions occurring are much larger than in methanol; and the volume decrease characterizing the lutidine reaction is *less* than that of pyridine. The results were that $\Delta\phi_V{}^0$ for pyridine is −95 ± 3, and for 2,6-lutidine it is −85 ± 3 cm^3/mol. Thus, the true numbers for the first two compounds in the last column of Table II are about 0.23 and 0.30. While these numbers are subject to the uncertainty introduced by ion association and perhaps even aggregation, they reinforce our belief that the trend shown in Table II is true. Parenthetically, they also provide strong evidence for the conclusion of many investigators, that the Menshutkin reaction in general is characterized by an early transition state. Thus, Kondo[25] has recently concluded on an entirely different basis that the charge development in the reaction of pyridine with benzyl chloride amounts to only 20% in the transition state.

It may be noted that the increase in volume per methylene group between 2,6-diisopropyl- and -*tert*-butylpyridine is anomalously large in methanol but not in acetone. This result strongly suggests that H-bonding between pyridines and methanol is still possible in the isopropyl case but no longer with *tert*-butyl.[26] If we accept the average increase in volume in methanol between the parent pyridine and the diisopropyl homolog as 17 cm^3/methylene group, the increase at *tert*-butyl is about 9 cm^3 larger. The volume change characterizing the formation of a hydrogen bond is generally accepted to be about −5 cm^3/mol;[27] in the precise measurements of Drickamer[28] for the H-bond of dilute 1-butanol in several inert solvents (based on the effect of pressure on the O–H stretching frequency), ΔV was found to be -4.64 cm^3/mol. The pyridines are evidently hydrogen bonded to two solvent molecules.

In summary, we conclude that the data presented here strongly suggest that the Hammond postulate may lie at the root of the special effect of pressure, to accelerate hindered reactions more than unhindered ones, or to put it another way, that this pressure effect is a manifestation of the postulate. It may be noted that other means have been put to use to test the postulate; thus, the chlorine isotope effect has been employed,[9] and Haberfield has supported it on the basis of thermochemical measurements.[29] It would seem, however, that the volume measurements described here are more directly related to the positions of the nuclei, and hence to the reaction coordinate.

Experimental Section

Materials. Pyridine,[30] 2,6-lutidine,[31] 2,6-diisopropylpyridine,[32] and 2,3,5,6-tetramethylpyridine[33] were prepared and purified as described in the references; in each case, the boiling or melting points as compared with literature values and NMR spectra were used as criteria of purity. The 2,6-di-*tert*-butylpyridine was obtained from Chemical Samples Co. and purified by fractional distillation. Methanol was dehydrated with magnesium and distilled. Acetone was treated with potassium permanganate and dried with potassium carbonate and Drierite before distillation.

2,6-Diethylpyridine. A solution of 60 g of glutaryl chloride in 180 ml of dry methylene chloride is added dropwise to a magnetically stirred solution of 110 g of ethylaluminum sesquichloride in 300 ml of dry methylene chloride at 0° (3 hr) under a blanket of dry nitrogen. The mixture is allowed to warm to room temperature and stirred 1 hr longer. The mixture is then slowly added to dilute sulfuric acid at 0°. The 3,7-nonanedione, obtained after extraction with ether and evaporation in 80%, is distilled [bp 128–130° (20 mm)] and recrystallized from *n*-hexane, mp 56° (lit.[34] 58°). A solution of this ketone (20 g) in 300 ml of ethanol is mixed with a solution of 40 g of hydroxylamine hydrochloride in 60 ml of water, and the mixture is refluxed under nitrogen for 6 hr; then it is concentrated under reduced pressure until the excess hydroxylamine hydrochloride crystallizes. The crystals are filtered off; the filtrate is neutralized with 4 *N* aqueous sodium hydroxide until the pH is about 8. The 2,6-diethylpyridine is obtained by steam distillation; the organic phase of distillate is separated, dried with anhydrous sodium sulfate, and distilled: yield 33%; bp 66.5–67.0° (12 mm) [lit.[35] 71–73° (17 mm)].

***N*-Methylpyridinium Iodide.** This salt was prepared by mixing pyridine with excess methyl iodide. The product was recrystallized from warm ethanol under nitrogen: white; mp 116.0–117.0° (lit.[36] 116.6–117.2°; lit.[37] 117°).

2,6,*N*-Trimethylpyridinium Iodide. This compound was prepared by dissolving 2,6-lutidine and methyl iodide in acetone and keeping the mixture at room temperature for several days. The product was recrystallized from warm methanol under nitrogen: very pale yellow; mp 235.9–236.8° (lit.[36] 236.8–238°; lit.[38] 238–240°).

1-Methyl-2,6-diethylpyridinium Iodide. This was prepared either by dissolving 2,6-diethylpyridine in methyl iodide[39] or in a methyl iodide–methanol mixture. The former mixture turned brown, and crystals started to precipitate after a day. The latter mixture turned yellow after a few days. It was diluted by anhydrous ether after 1 month, and the yellow crystals formed were dissolved in ethanol at room temperature and made to crystallize by adding anhydrous ether. All operations were done under nitrogen: white; mp 140.8–141.5° (lit.[39] 142°). The purified crystals turned partially yellow after brief exposure to air, and the decomposition continued even under nitrogen and in the absence of light; the crystals finally became brown after a few days. It was not possible to repurify those crystals by simple recrystallization. Activated charcoal also induced decomposition.

The brown crystals isolated from the former reaction mixture and the impure crystals mentioned above were purified by column chromatography (silica gel–acetonitrile). The brown impurity was removed completely, and other remaining impurities were thereafter easily removed by recrystallization from ethanol–ether: white; mp 141.8–142.8°.

1-Methyl-2,6-diisopropylpyridinium Iodide. This was prepared by treating 2,6-diisopropylpyridine with methyl iodide at room temperature.[39] After a period of a few months to 1 year, yellow crystals were isolated from the reaction mixture. The purification procedure consisted of dissolving the raw product in pure acetone, cooling the solution by Dry Ice, and adding anhydrous ether. The crystals obtained were white, but turned to very pale yellow after a few days, mp 161.2–162.0° (lit.[39] 118.5°).

In view of the melting-point discrepancy, ir, uv–visible light, and NMR spectra were recorded.

As a further criterion of purity, equivalent weights were determined by titration with silver nitrate. The equivalence point was determined potentiometrically. For each of the four salts described, the difference with the calculated value was 0.4 or less.

Density Measurements. Each salt was taken into a 25-ml volumetric flask and weighed quickly and diluted. The density measurements were done with Sprengel pycnometers of about 14-ml capacity. They were calibrated by means of doubly distilled water. The temperature was 25.000 ± 0.002°. The measurements were made on days of low relative humidity; the weights were frequently calibrated.

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References and Notes

(1) Paper XXX in the Series: Kinetics of Reactions in Solutions under Pressure. For the preceding papers, see W. J. le Noble and Y. S. Chang, *J. Am. Chem. Soc.*, **94**, 5402 (1972); *J. Chem. Educ.*, **50**, 418 (1973). The work described here was presented (by T.A.) in part at the Second Regional Meeting of AIRAPT, Kyoto, Japan, 1972.

(2) For review, see W. J. le Noble, *Prog. Phys. Org. Chem.*, **5**, 207 (1967); G. Kohnstam, *Prog. React. Kinet.*, **5**, 335 (1970).

(3) ΔV^{*} may also be positive, and many examples of this are known; see ref 2.

(4) Y. Okamoto and Y. Shimakawa, *J. Org. Chem.*, **35**, 3752 (1970), and other work quoted there.

(5) W. J. le Noble and Y. Ogo, *Tetrahedron*, **26**, 4119 (1970).

(6) M. G. Gonikberg, *Russ. J. Phys. Chem.*, **37**, 247 (1963), and earlier papers quoted therein.

(7) And vice versa! In one remarkable switch of the usual sequence of calculation and experiment, the immersal of Stuart–Briegleb models in graduate cylinders was used to arrive at a value for the effective radius of a *tert*-butyl group [N. I. Prokhorova, B. S. El'yanov, and M. G. Gonikberg, *Proc. Acad. Sci. USSR, Chem. Sect.* 256 (1967)]. The procedure was found to work satisfactorily by calibration with a similar model for methane.

(8) See the survey by S. D. Hamann in "High Pressure Physics and Chemistry", Vol. II, R. S. Bradley, Ed., Academic Press, New York, N.Y., 1963, Chapter 8.

(9) C. G. Swain and N. D. Hershey, *J. Am. Chem. Soc.*, **94**, 1901 (1972), and references therein.

(10) K. E. Weale, "Chemical Reactions at High Pressures", Spar, London, 1967, Chapter 6. On the other hand, the *differences* in activation volume between hindered and unhindered Menshutkin reactions are indeed relatively insensitive to solvent.[5]

(11) F. Westheimer in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, Chapter 12.

(12) J. Hine, *J. Am. Chem. Soc.*, **88**, 5525 (1966). For a recent discussion, see O. S. Tee and K. Yates, ibid., **94**, 3074 (1972). If steric hindrance were forcing a more circuitous approach of the reagent molecules, it would intuitively seem that the effect of this on the transition-state volume must be enlargement rather than diminution.

(13) R. Hoffmann, R. Gleiter, and F. B. Mallory, *J. Am. Chem. Soc.*, **92**, 1460 (1970).

(14) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970.

(15) R. A. Grieger, C. Chaudoir, and C. A. Eckert, *Ind. Eng. Chem.*, **10**, 24 (1971).

(16) F. J. Millero, *Rev. Sci. Instrum.*, **38**, 1441 (1967); A. B. Lamb and R. E. Lee, *J. Am. Chem. Soc.*, **35**, 1666 (1913).

(17) O. Redlich and J. Bigeleisen, *J. Am. Chem. Soc.*, **64**, 758 (1942); F. Vaslow, *J. Phys. Chem.*, **70**, 2286 (1966).

(18) For a recent example, see D. D. McDonald and J. B. Hyne, *Can. J. Chem.*, **48**, 2416 (1970).

(19) C. L. de Ligny, P. F. M. Luykx, M. Rehbach, and A. A. Wienecke, *Recl. Trav. Chim. Pays-Bas*, **79**, 699 (1960); R. L. Kay, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.*, **69**, 4208 (1965).

(20) For a review, see F. J. Millero, *Chem. Rev.*, **71**, 147 (1971).

(21) O. Redlich and D. M. Meyer, *Chem. Rev.*, **64**, 221 (1964). Alternatively, Masson's equation may be used, which omits the $b_V C$ term. S_V is then found by means of a plot of ϕ_V vs. $C^{1/2}$. In our experiments, the values of $\phi_V{}^0$ as found by means of these two equations were the same within the limit of error in every case.

(22) J. Padova and I. Abrahamer, *J. Phys. Chem.*, **71**, 2112 (1967).

(23) W. J. le Noble and T. Asano, *J. Org. Chem.*, in press.

(24) Y. Okamoto, *J. Am. Chem. Soc.*, **90**, 5639 (1968); Y. Okamoto and K. I. Lee, Abstracts, 168th Meeting of the American Chemical Society, Atlantic City, N.J., Sept 1974, ORGN 046.
(25) Y. Kondo, M. Ohnishi, and N. Tokura, *Bull. Chem. Soc. Jpn.*, **45**, 3579 (1972).
(26) The same conclusion has recently been reached on another basis: H. Knötzinger, *Surf. Sci.*, **41**, 339 (1974).
(27) E. Whalley, *Adv. Phys. Org. Chem.*, **2**, 93 (1964).
(28) E. Fishman and H. G. Drickamer, *J. Chem. Phys.*, **24**, 548 (1956).
(29) P. Haberfield, A. Nudelman, A. Bloom, R. Romm, and H. Ginsberg, *J. Org. Chem.*, **36**, 1792 (1971).
(30) J. G. Heap, W. J. Jones, and J. B. Speakman, *J. Am. Chem. Soc.*, **43**, 1936 (1921). The pyridine-zinc chloride complex has a melting point of 150-151°.
(31) W. Koenigs and G. Happe, *Chem. Ber.*, **36**, 2904 (1903).
(32) H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **88**, 986 (1966).
(33) P. F. G. Praill and A. L. Whitear, *Proc. Chem. Soc., London*, 312 (1959).
(34) H. Reinhechel and R. Genslke, *J. Prakt. Chem.*, **37**, 214 (1968).
(35) E. E. Blaise and M. Montagne, *C. R. Acad. Sci.*, **180**, 1760 (1925).
(36) E. M. Kosower and J. A. Skorcz, *J. Am. Chem. Soc.*, **82**, 2195 (1960).
(37) A. B. Prescott, *J. Am. Chem. Soc.*, **18**, 91 (1896).
(38) E. M. Kosower and P. E. Klinedinst, *J. Am. Chem. Soc.*, **78**, 3493 (1956).
(39) R. Lukes and M. Pergál, *Chem. Listy*, **52**, 68 (1958).

Extended Hückel Calculations on Benzylmercuric Bromide. Evidence for σ–π Conjugation

Paul A. Scherr, Milton D. Glick, John H. Siefert, and Robert D. Bach*

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received April 16, 1974*

Abstract: Extended Hückel molecular orbital calculations suggest that benzylmercuric bromide exists in a conformation where the polarizable carbon-mercury bond can interact with the π system of the aromatic ring. Theoretical evidence for significant σ-π stabilization of the ortho and para Wheland intermediates involved in proton exchange of this mercurial is presented.

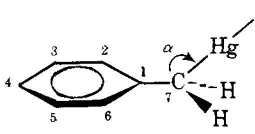
It has been established for some time that the R_3MCH_2 group (M = Si, Ge, Sn, Pb) has a greater electron-releasing capacity than the R_3M moiety.[1] On the basis of charge-transfer frequencies of phenyl-substituted organometallic compounds, it has been suggested that the $-CH_2Sn(C_6H_5)_3$ group is as activating as a methoxy group, and the $-CH_2SnMe_3$ group is almost as effective as an amino substituent.[2] The $-CH_2Fe(CO)_2$-π-C_5H_5 group is also more highly activating toward aromatic electrophilic substitution than is the methoxy group.[3] Both chemical[4] and spectroscopic[5] evidence indicates that this enhanced reactivity is derived from σ-π conjugation of the carbon-metal bond with the neighboring cationic center. Moreover, recent theoretical evidence supports carbon-metal hyperconjugation in group IV allyl organometallic compounds[6a-c] and allylmercuric halides.[6d] On the basis of CNDO/2 calculations, Jones[6e] has suggested that d orbitals are more important than hyperconjugative p-pπ interaction in the ground state with *m*-trimethylsilyl-*N*,*N*-dimethylaniline. Extended Hückel (EH) calculations on Si, Ge, and Pb allyl derivatives give essentially identical results regardless of whether inner d orbitals and/or outer d orbitals are included.[6c] Our molecular orbital calculations on the acid cleavage of allylmercuric bromide strongly suggested that the degree of σ-π stabilization in the transition state for this acid cleavage was dependent upon the conformation of the allymercuric halide. These data were in excellent agreement with experimental evidence of Traylor[2,5c] and Pitt[4c] who established the necessity for the coplanarity of the C-M bond and the axis of the electron-deficient π orbital. In these calculations, the d-orbital participation in the ground state and in the transition state for protolysis was also found to be minimal. In a study of the deuteriodemetalation of benzylmercuric chloride with DCl in dioxane, Reutov[4c] reported almost exclusive incorporation of deuterium in the ortho position of the aromatic ring. This was attributed to σ-π conjugation and a favored six-member cyclic transition state. Traylor[7] has also reported incorporation of deuterium in the aromatic ring when dibenzylmercury was treated with trifluoroacetic acid-*d* in chloroform. The ortho to para rate ratio for exchange, however, was 0.84, and a σ-π conjugation mechanism was again invoked. We now report extended Hückel molecular orbital calculations which support the σ-π conjugation mechanism for the protonation-deprotonation of benzylmercury compounds.

Experimental Section

Extended Hückel molecular orbital calculations, as developed by Hoffmann,[8] were carried out as previously described.[6d,9] The aromatic ring was located in the *xy* plane. Bond angles for sp^2 and sp^3 carbon atoms were taken as 120 and 109.5°, respectively. Carbon-carbon bond distances were taken as 1.395 (aromatic) and 1.52 Å, while the C-Br, C-Hg, and Hg-Br bond distances were 2.00, 2.074, and 2.406 Å, respectively. Carbon-hydrogen bond distances were taken as 1.084 (ring) and 1.09 Å (benzylic), except for a carbon-proton bond distance of 1.2 Å in the transition states for proton addition to the benzene ring. The H-C-H bond angle in the Wheland intermediates was 109.5° with a C-H bond distance of 1.084 Å. The H-Cl bond distance in the HCl complex (**8**) with benzylmercuric chloride was 1.2 Å, and the Cl-Hg bond distance was taken as 2.22 Å. The hydrogen was 1.2 Å above the ortho carbon with a C_2-H-Cl bond angle of 120°. The Hg-O bond distance in the aquocomplex **9** was 2.13 Å, and the C_7-Hg-Cl bond angle was 120°. The H-O-H bond angle was 104.5°, and the O-H bond distances were 0.96 and 1.27 Å with the latter hydrogen being 1.08 Å above the ortho carbon with a C_2-H-O bond angle of 120°.

Results and Discussion

We first directed our attention toward calculating the preferred conformation of benzylmercuric bromide in order to compare these results with those obtained in allymercuric bromide.[6d] Extended Hückel molecular orbital calculations suggest that in the ground state benzylmercuric bromide is more stable in conformation **1** (β = 90°), where the polari-



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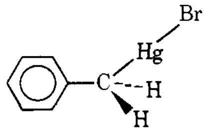

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