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Internal Energy Distributions and the Fragmentation of Gaseous Organic Ions. Dissociation of Ions Produced by Electron Impact on 4-Methylbenzil[1]

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Abstract: The 70-eV mass spectrum of 4-methylbenzil (1-(4-methylphenyl)-2-phenylethane-1,2-dione) has been rationalized by energy deposition functions estimated by the second derivative technique. Cleavage of the C1–C2 bond in the molecular ion, *m/e* 224, produces either the 4-methylbenzoyl ion, *m/e* 119, or the benzoyl ion, *m/e* 105. These ions fragment with loss of CO forming ions of *m/e* 91 and 77, respectively. Since high internal energies are required, fragmentations of these ions were not investigated. Thermochemical considerations indicate that formation of the benzoyl and 4-methylbenzoyl radicals accompanies production of ions *m/e* 119 and 105, respectively. Some of the evidence suggests that fragmentation occurs from more than one electronic state of the molecular ion. However, the variation in the ratio of rate constants for formation of ions of *m/e* 105 and 119 with internal energy suggests that energy randomization is essentially complete in the molecular ion prior to its decomposition up to an internal energy of *ca.* 4.8 eV. The relative rate constant plot at higher-internal energies is discussed in terms of autoionization and isomerization of the molecular ion. The breakdown graph and energy deposition function derived from the second derivative of the ionization efficiency are presented. The standard deviations in the first derivatives are interpreted in terms of shot noise, and standard deviations in the second derivatives are computed.

The assumption that the mass spectrum of a polyatomic molecule results from competing and consecutive unimolecular reactions of the internally excited molecular ion led to the development of the quasi-equilibrium or statistical theory.[3] The rate constants, $k_i(E)$, for each reaction calculated as a function of the internal energy of the molecular ion[3,4] are used to compute a breakdown graph which is folded into the internal energy distribution function, $P(E)$, to yield the mass spectrum.[5] Prediction (analysis) of a mass spectrum requires knowledge of the $k_i(E)$ and of $P(E)$. The theory has been applied to the mass spectra of "small" organic molecules.[3,5,6] Comparison of experimental ion intensities with those computed from calculated values of $k_i(E)$ and an assumed function for $P(E)$ constitutes one test of the theory.[6a–f] An experimental approach would involve the determination of $P(E)$, and this has been approximated by measurement of the energy deposition function, $P(\mathrm{ED})$.[7] In this study we have employed the second derivative of the total ionization produced by electron impact[8] to estimate $P(\mathrm{ED})$.[6i] Breakdown graphs can be obtained by charge exchange experi-

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ments,[9] from photoion–photoelectron coincidence mass spectrometry,[10] and from the appropriate derivative[8] of the individual ion intensities.[6i,j,11] Agreement has been found between such experimental data and the results of detailed calculations on the reactions of the propane molecular ion.[12]

Reasonable success has been achieved in partial calculation of the mass spectra of complex organic molecules using a modified form of the original statistical theory and assuming a functional form of $P(E)$.[13] Except for a series of ring-substituted 1,2-diphenylethanes,[14] little attention has been devoted to determination of the energy distribution function of molecular ions formed from complex organic molecules. Yet, a prerequisite for an understanding of the apparent substituent effect upon the energetics of competitive fragmentation of such molecular ions in the 70-eV mass spectrum is knowledge of the effect of substituents on the energy deposition function. A reasonable estimate of P(ED) should be obtainable from the second derivative of the electron-impact-induced ionization efficiency curve,[8,6i] even though a linear threshold law may not be valid for energies considerably in excess of threshold value.[7] As the initial part of research utilizing the second derivative method to obtain such information, we communicate results obtained for the electron-impact-induced ionization and fragmentation of 4-methylbenzil (I), *i.e.*, 1-(4-methylphenyl)-2-phenylethane-1,2-dione.

Experimental Section

4-Methylbenzil (I). 4-Methylphenyl benzyl ketone was prepared from bis(4-methylphenyl)cadmium[15] and phenylacetyl chloride[16] by standard techniques.[17] 4-Methylphenyl benzyl ketone was oxidized to I with selenium dioxide.[18] Crude I was distilled at 132.5° at 0.27 mm twice and then recrystallized from *n*-pentane, mp 28.8–29° (lit.[19] mp 31°).

Instrumentation. Mass spectra and the first derivative of the ionization efficiency were determined with the LKB 9000P mass spectrometer. Xenon was introduced into the ion source *via* the direct probe as modified for gas analysis. To maintain uniform sample pressure, I was introduced into the ion source *via* the gas chromatograph inlet and separator systems. Temperatures were as follows: oven 135°, separators 150°, ion source 310°. The trap current was maintained constant at 20 μA and the electron shield was at zero potential with respect to the filament. Except for spectra recorded at 70 eV, both spectra and dI/dE data were obtained with the extraction plates near the block potential. To maximize peak flatness and ion intensity, the source and collector slits were 0.1 and 0.9 mm, respectively. First derivative data were basically obtained by published techniques.[20] The modulation frequency and voltage were 595 Hz and 0.075 V peak-to-peak, respectively. The dI/dE data were read from a Beckman Model 5571/1 electronic counter driven by the output from a Matrix Model 1612 voltage-to-frequency converter. The electron energy was measured with a Science Metrics 1611 digital voltmeter and was manually increased in 0.100 ± 0.002 eV steps. The lock-in-amplifier was a Keithley Model 840. Preliminary measurements were made on a RMU-6 mass spectrometer.

Numerical Treatment of Experimental Data and Error Analysis. All mass spectra were corrected for naturally occurring heavy isotopes of carbon, hydrogen, and oxygen.[21] The electron energy scale was calibrated using xenon. The second derivative of the ionization efficiency (SDIE) curve for xenon was obtained by differentiating the experimental dI/dE values without numerical smoothing and exhibited a second maximum at 12.80 ± 0.05 eV, which is caused by the 6d autoionizing state.[20] During the experiments the full-width half-maximum (FWHM) of the xenon SDIE curve was at 0.42–0.55 eV or 0.63–0.74 eV depending on whether 0.020- or 0.030-in. rhenium ribbon was used for the filament.

Within the limits of noise the maximum value of dI/dE for each ion pertinent to the study of I was essentially constant for *ca.* 3 eV, beyond which a slow decrease was observed. For purposes of differentiation, the average of these values for each ion was taken as the maximum value for each first derivative curve. For each ion, the experimental dI/dE values were numerically smoothed twice using subroutine SE-15,[22] and the resultant values were taken to constitute the first derivative of the ionization efficiency (FDIE) curve.

The d^2I/dE^2 value at the ith voltage V_i was computed using the doubly smoothed dI/dE values $y(\mathrm{d}S)_{i+k}$, where $k = \pm1, \pm2$, and ±3 by eq 1 and h equals the energy interval 0.100 eV.[23] Equation 1 can be derived by differentiating the polynomial of degree six

$$F''(V_i) = \frac{1}{h}\left\{\frac{3[y(\mathrm{d}S)_{i+1} - y(\mathrm{d}S)_{i-1}]}{4} - \frac{3[y(\mathrm{d}S)_{i+2} - y(\mathrm{d}S)_{i-2}]}{20} + \frac{y(\mathrm{d}S)_{i+3} - y(\mathrm{d}S)_{i-3}}{60}\right\} \quad (1)$$

which has been fitted to seven consecutive points and solving for the coefficients in eq 2. The $F''(V_i)$ values were then smoothed

$$F''(V_i) = \frac{A[y(\mathrm{d}S)_{i+1} - y(\mathrm{d}S)_{i-1}]}{2h} - \frac{B[y(\mathrm{d}S)_{i+2} - y(\mathrm{d}S)_{i-2}]}{4h} + \frac{C[y(\mathrm{d}S)_{i+3} - y(\mathrm{d}S)_{i-3}]}{6h} \quad (2)$$

once, *vide supra*, to obtain the SDIE curve.

The true standard deviation (σ_T) of a single dI/dE measurement is determined by the absolute ion intensity (shot noise), the lock-in-amplifier time constant, the integration time, and the multiplier noise contribution.[24] For a collection of dI/dE points at a given electron voltage, the experimental standard deviation (σ_{exptl}) will be a function also of sample size and the sampling rate.[24] For example, the dI/dE data for m/e 224 was obtained with a time constant of 100 sec and an integration time of 1 sec. The average sample size was about 20 points and the sampling rate was *ca.* 1 point per 2 sec. The σ_{exptl} for this sample size is approximately 35% σ_T.[24] Since successive measurements of dI/dE are not statistically independent, a relatively large sample was obtained at each of three points along each dI/dE curve under the same instrumental conditions and sample pressure used to obtain the dI/dE data, in an attempt experimentally to estimate σ_T and its variation with electron energy. For each data collection so obtained σ was computed for increasing numbers of consecutive data points in the sample. For example, 180 points taken with a sampling interval of 11 sec at 8.65, 11.25, and 12.85 eV at m/e 224 were sufficient to provide reasonable estimates of σ_T. In this instance a larger sampling interval was used to decrease the number of data points required. As expected, σ fluctuated widely for small data sets. For each ion

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Table I. Standard Deviations in the FDIE and SDIE Curves as a Function of Electron Energy

		Per cent				Per cent	
m/e	eV[a]	$\sigma_{\mathrm{T(exptl)}}$ dI/dE[b,c]	σ d^2I/dE^2[d]	m/e	eV[a]	$\sigma_{\mathrm{T(exptl)}}$ dI/dE[b,c]	σ d^2I/dE^2
224	8.65	5.68	5.9	91	13.05	3.78	5.9
	11.25	3.21	15.9		15.05	1.61	6.0
	12.85	3.52	52.2		18.05	1.69	18.7
119	9.55	1.00	5.1	77	14.05	2.84	5.7
	11.55	1.18	6.5		17.05	2.59	9.6
	13.55	0.617	6.9		19.55	1.51	13.1
105	9.85	5.00	6.7				
	12.05	1.96	6.6				
	16.55	2.11	18.2				

[a] Calibrated. [b] The lock-in-amplifier time constant (sec), integration time (sec), number of points taken to estimate σ, and the multiplier gains are: for m/e 224, 100, 1, 80, and 1.20×10^4; m/e 119, 30, 1, 60, and 1.31×10^4; m/e 105, 30, 1, 60, and 1.35×10^4; m/e 91, 30, 1, 60, and 1.37×10^4; m/e 77, 30, 10, 60, and 1.50×10^4. The sampling interval was 11 sec. [c] Experimental dI/dE values normalized to the maximum value of dI/dE for m/e 119 equal to 100 in order of increasing electron energy are for m/e 224, 1.780×10^{-1}, 1.027, and 1.261; m/e 119, 15.48, 57.89, and 94.46; m/e 105, 6.759×10^{-1}, 4.399, and 14.35; m/e 91, 9.634×10^{-1}, 8.086, and 25.75; m/e 77, 3.058×10^{-1}, 2.902, and 5.395. [d] The d^2I/dE^2 values based upon the normalized dI/dE values in order of increasing electron energy are for m/e 224, 4.123×10^{-1}, 2.741×10^{-1}, and 1.075×10^{-1}; m/e 119, 21.48, 21.04, and 15.57; m/e 105, 9.548×10^{-1}, 2.653, and 2.176; m/e 91, 1.446, 4.922, and 3.033; m/e 77, 3.058×10^{-1}, 1.148, and 8.428×10^{-1}.

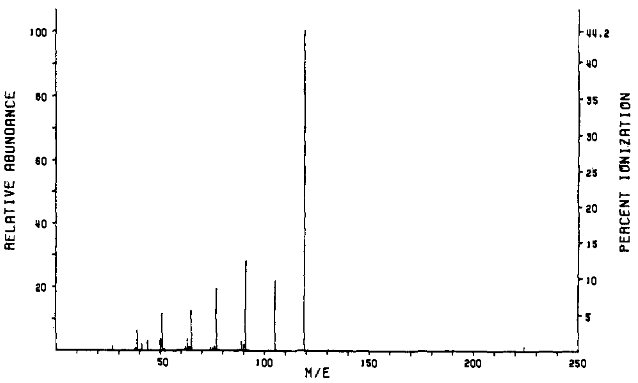
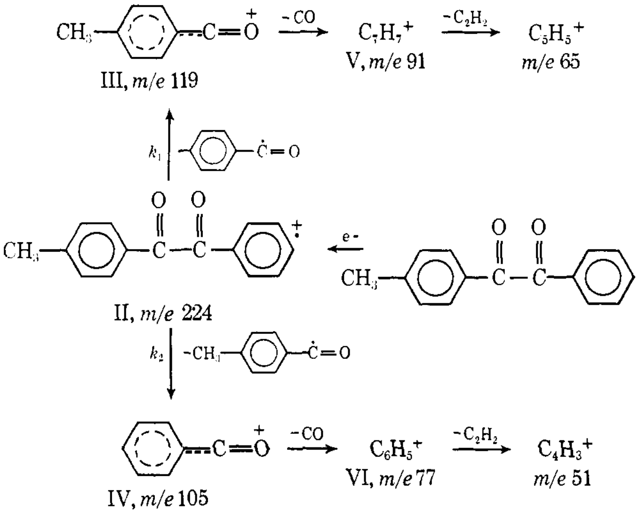


Figure 1. The 70-eV mass spectrum of I.

Scheme I



III, m/e 119

V, m/e 91

m/e 65

II, m/e 224

IV, m/e 105

VI, m/e 77

m/e 51

these experimental estimates of σ_{T}, $\sigma_{\mathrm{T(exptl)}}$, at three values of the electron energy are tabulated in Table I. Since these values are within a factor of 2 of the values predicted from analytical consideration of the shot noise,[24] it is reasonable to conclude that shot noise is the major contributor to deviations in dI/dE and that the estimates of σ_{T} in Table I for each ion are reasonable. Finally, theory predicts that σ for dI/dE values will increase as the $^1/_2$ power of the absolute ion intensity.[24] In conformity to this, for any ion the ratio of $\sigma_{\mathrm{T(exptl)}}$ values at two electron voltages reasonably approximates the $^1/_2$ power of the ratio of the corresponding ion intensities; *e.g.*, these two ratios are respectively: for m/e 224 at 8.65/11.25 eV 0.34 and 0.19, at 11.25/12.85 eV 0.72 and 0.71; for m/e 119 at 9.55/11.55 eV 0.23 and 0.30, at 11.55/13.55 eV 1.17 and 0.59; for m/e 105 at 9.85/12.05 eV 0.41 and 0.26, at 12.05/16.55 eV 0.27 and 0.32.

The standard deviation in d^2I/dE^2 values was computed in the following manner. Let y_i and $y(S)_i$ represent the experimental and once smoothed dI/dE values for a given ion at the ith electron voltage. The smoothing routine performs a moving five-point average. The $y(S)_i$ values are given in terms of the y_i values by eq 3. Except

$$y(S)_i = a_1y_{i-2} + a_2y_{i-1} + a_3y_i + a_4y_{i+1} + a_5y_{i+2} \quad (3)$$

for the end-point regions, the coefficients a_1 to a_5 in eq 3 have the value $^1/_5$. Zero values were added below onset and the average maximum was extended to eliminate the end-point effects in SE-15. The $y(\mathrm{d}S)_i$ are obtained from $y(S)_i$ by application of eq 3 to $y(S)_i$. Clearly, the $y(\mathrm{d}S)_i$ can be expressed in terms of the y_i The expression so obtained is given in eq 4. Thus two five-point smoothing operations of dI/dE are equivalent to one nine-point such smoothing, where the coefficients of the latter are determined by those of the former.

$$y(\mathrm{d}S)_i = \sum_{k=-4}^{k=+4} b_ky_{i+k} \quad (4)$$

$$b_k = (5 - |k|)/25$$

$$k = 0 \pm 1, \ldots, \pm 4$$

Similarly, the $y(\mathrm{d}S)_i$ in eq 1 can be expressed in terms of the y_i. The desired function $F''(V_i)$ can be obtained by convoluting the coefficients of eq 4 into those of eq 3. An antisymmetric set of 15 coefficients is obtained whose values are $-C_{-7} = C_7 = 1/1500$, $-C_{-6} = C_6 = -7/1500$, $-C_{-5} = C_5 = 30/1500$, $-C_{-4} = C_4 = 67/1500$, $-C_{-3} = C_3 = 59/1500$, $-C_{-2} = C_2 = 58/1500$, $-C_{-1} = C_1 = 74/1500$, $C_0 = 0$. Therefore, d^2I/dE^2 at the ith eV is formally given by eq 5. The contribution to σ^2 in $F''(V_i)$ from the $i + j$

$$F''(V_i) = \frac{1}{h}\sum_{j=-7}^{j=+7} C_jd_{i+j} \quad (5)$$

value of dI/dE is $C^2{}_j\sigma^2{}_{i+j}/h^2$.[25] The total contribution is $(1/h^2)\Sigma_{j=-7}^{j=7}C^2{}_j\sigma^2{}_{i+j}$. For ease of calculation the standard deviation of dI/dE was assumed constant over the range of dI/dE values required to calculate a d^2I/dE^2 value. The contribution to σ^2 due to the uncertainty in the energy interval h is given by evaluation of $[\partial F''(V_i)/\partial h]^2\sigma_h{}^2$. Because of possible variations in the mean electron energy due to changes in the filament temperature, the uncertainty in h was increased from 0.002 to 0.005 eV. The standard deviation in d^2I/dE^2 is thus given by eq 6 where $\sigma(y_i)$ is the per cent

$$\sigma(F''(V_i)) = \frac{1}{h}\left\{F''(V_i)^2\sigma_h{}^2 + 0.015787\left[\frac{\sigma(y_i)y_i}{100}\right]^2\right\}^{1/2} \quad (6)$$

standard deviation in dI/dE. The $\sigma(y_i)$ values and the data in footnotes *c* and *d* of Table I lead to the calculated per cent standard deviations of d^2I/dE^2 for each ion given in Table I. For a given ion, the deviation of d^2I/dE^2 is dependent on the absolute ion intensity (related to dI/dE) and, therefore, increases with increasing electron energy. The standard deviation is dominated at low-electron voltage by the uncertainty in the energy increment and at high-electron voltage by uncertainty in dI/dE. For each ion a minimum of four sets of dI/dE data were recorded over a time of some 6 months. The fact that deviations in the d^2I/dE^2 values between sets were, except as discussed below, within the estimated uncer-

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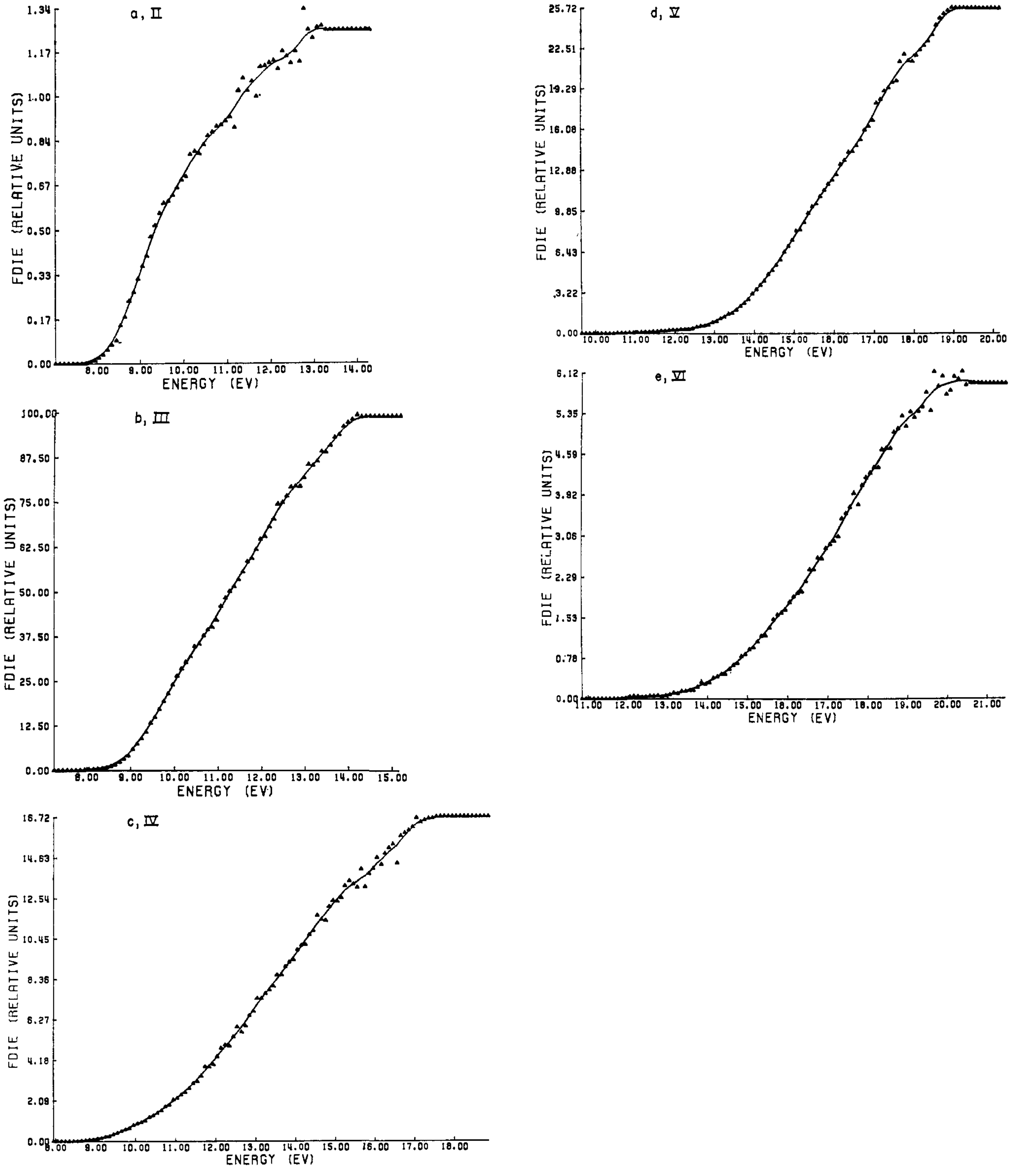

Figure 2. Plots of experimental d*I*/d*E* and FDIE values for II through VI *vs.* electron energy.

tainties helps validate the per cent uncertainties in Table I. Deviations in d^2I/dE^2 would be expected to reflect in part differences in the electron energy spread. Excess spread in the d^2I/dE^2 curves at low-electron voltage could be accounted for by changes in the width of the electron energy distribution as determined by the FWHM of the xenon SDIE curves.

Results and Discussion

Fragmentation Scheme. The 70-eV mass spectrum of I is reproduced in Figure 1. The per cent ion abundances in Table II show that the mass spectrum of I at 70 eV is dominated by seven ions and below 20 eV consists completely of seven ions. Metastable peaks were observed for the following transi-

Table II. Per Cent Ion Abundances in the Mass Spectra of 4-Methylbenzil as a Function of Electron Energy

	Per cent ion abundance for *m/e*							
eV[a]	224	119	105	91	77	65	51	Total
70	0.6	44.5	9.5	12.4	8.6	5.5	5.0	86.1
20	1.2	72.5	11.8	11.0	2.7	0.5	0.0	99.7
15	1.7	86.5	8.8	2.7	0.3	0.0	0.0	100.0

[a] Calibrated.

tions: m/e 119^+ to $91^+ + 28$ ($m^* = 69.6$), m/e 105^+ to $77^+ + 28$ ($m^* = 56.5$), m/e 91^+ to $65^+ + 26$ ($m^* = 46.4$), and m/e 77^+ to $51^+ + 26$ ($m^* = 33.8$). In harmony with these data and results from related systems,[26a,b] Scheme I is proposed to account for the principal features of the mass spectrum of I. The data in Table II reveal that the ions at m/e 119 (III) and 105 (IV), formed *via* competitive dissociations of the C1–C2 bond in the molecular ion of I (II), and the ions at m/e 91 (V) and 77 (VI), produced by loss of CO from III and IV, respectively, account for 75.7 and 99.2% of the total ion intensity at 70 and 20 eV, respectively. Since other fragmentations have high-energy requirements, the energy dependence of these other processes was not investigated.

For II through VI Figure 2 presents one set of FDIE curves normalized to the maximum value of FDIE for III equal to 100 and the experimental dI/dE points. The FDIE curves in Figure 2 were differentiated to obtain the d^2I/dE^2 values at each electron energy. The results obtained for each ion are plotted in Figure 3 as a function of the electron energy minus the ionization potential, which represents the energy deposition for d^2I/dE^2. The SDIE curves in Figure 3 represent the line drawn through the points obtained from a single smoothing of the d^2I/dE^2 values.

Inferences on Conformation of I from Relative Ionization Potentials. The second derivative technique yields values of 9.05 ± 0.10 and 8.86 ± 0.15 eV for ionization potentials of I and benzil (VII), 1,2-diphenylethane-1,2-dione. The result for VII is in reasonable agreement with the literature value of 8.78 eV.[26a]

The experimental ionization potential for I is larger than the thermodynamically calculated (see Appendix) value of 8.61 ± 0.17 eV. This difference, which is slightly outside of the combined errors, may result from the tendency of the second derivative technique to overestimate ionization and appearance potentials by as much as 0.3 eV even when the SDIE curves show a clear maximum.[26c] The n → π* transitions for VII,[27] I,[28] and 1,2-bis(4-methylphenyl)ethane-1,2-dione[29] (VIII) have similar energies. Thus, although the orbital involved in electron removal is unknown, these results parallel by Koopman's theorem[30] the similar first ionization potentials of I and VII. Substitution of a methyl group for a *p*-hydrogen atom in VII to arrive at I is indicated to produce only a small perturbation on the energy of the ground state of the molecular ion relative to that of the molecule.

The ionization potentials of I and VII deserve comment. In the condensed phase at room temperature, the two planar benzoyl groups in I, VII, and VIII lie in planes approximately at right angles to each other.[27-29] For example, the ultraviolet spectra of VII and a number of its derivatives resemble those of benzaldehyde (IX) and its corresponding derivatives.[27a] Thus, ionization would be expected to involve a transition from the ground state of the neutral molecule in a skew conformation to the ground ionic state in the same conformation. By this reasoning the first ionization potentials of VII and I would be similar to those for IX (9.51[31]–9.80[32] eV by photon impact) and 4-methylbenzaldehyde, IX-4 (9.35 eV[33] by electron impact), whereas in fact VII and I have lower first ionization potentials than the benzaldehydes do. However, the electron energy levels of the ground states of I and VII will depend upon conformation. For example, the energy of the n → π* transition of 1,2-bis(2,4,6-trimethylphenyl)ethane-1,2-dione is indicative of a coplanar trans arrangement of the carbonyl groups with each aromatic ring twisted out of the plane of its carbonyl.[27b] In a completely planar conformation, the cross conjugation of the carbonyl groups allows interaction of the aromatic rings. Similarly, this conclusion should be valid for ionic states of these molecules. For example, analysis of the absorption and phosphorescence spectra of VII, I, and related molecules provides evidence that a coplanar trans conformation constitutes the lowest excited triplet state.[28,34] Finally, the interaction of the π orbitals of each carbonyl group in planar ethane-1,2-dione and nearly planar butane-2,3-dione is reflected (a) in the energy of the n → π* transitions[27c,34] and (b) assumably in the lower ionization potential of these diones (9.48[35] and 9.25 eV[31], respectively) compared with formaldehyde (10.87 eV[31]) and acetone (9.69 eV[31]). Thus, a wholly planar conformation of I and VII should by analogy have a lower ionization potential than a skew structure. Although the high-temperature ultraviolet spectra of I and VII have not been reported, it seems likely that the average molecular temperature prior to electron impact, *i.e.*, 135–310°, is sufficient to affect the conformational distribution. For example, the marked temperature dependence of the ultraviolet spectrum of oxalyl chloride has been discussed in such terms.[36] Thus, the reduction in the ionization potentials of I and VII over those of IX-4 and IX is at least qualitatively consistent with vertical transitions occurring from the planar conformation. These considerations need further attention both experimentally and theoretically.

Thermodynamics of Fragmentation. Concerted rupture of the C1–C2 and of the C_6H_5–C1 or of the $CH_3C_6H_4$–C2 bonds in II constitutes an alternative to the one-bond rupture mechanism in Scheme I for formation of III and IV, respectively (see eq 7 and 8). For III,

$$\mathrm{II} \longrightarrow \mathrm{III} + \mathrm{CO} + \mathrm{C_6H_5}\cdot \tag{7}$$

$$\mathrm{II} \longrightarrow \mathrm{IV} + \mathrm{CO} + \mathrm{CH_3C_6H_4}\cdot \tag{8}$$

appearance potentials of 9.73 ± 0.18 and 10.58 ± 0.23 eV are calculated (see Appendix) for the one-

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(26) For a discussion of the mass spectrum of benzil from a thermodynamic viewpoint see: (a) P. Natalis and J. L. Franklin, *J. Phys. Chem.*, **69**, 2943 (1965); (b) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, Chapters 1 and 3; (c) G. G. Meisels and B. G. Giessner, *Int. J. Spectrom. Ion Phys.*, **7**, 489 (1971).

(27) (a) N. J. Leonard, R. T. Rapala, H. L. Herzog, and E. R. Blout, *J. Amer. Chem. Soc.*, **71**, 2997 (1949); (b) N. J. Leonard and E. R. Blout, *ibid.*, **72**, 484 (1950); (c) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, New York, N. Y., 1967, Chapter 21.

(28) Y. Ogata, K. Takagi, and Y. Fujii, *J. Org. Chem.*, **37**, 4026 (1972).

(29) K. Maruyama, K. Ono, and J. Osugi, *Bull. Chem. Soc. Jap.*, **45**, 847 (1972).

(30) T. Koopman, *Physica (Utrecht)*, **1**, 104 (1933).

(31) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

(32) A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc. B*, 22 (1968).

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(35) R. I. Reed and J. C. D. Brand, *Trans. Faraday Soc.*, **54**, 478 (1958).

(36) J. W. Sidman, *J. Amer. Chem. Soc.*, **78**, 1527 (1956).

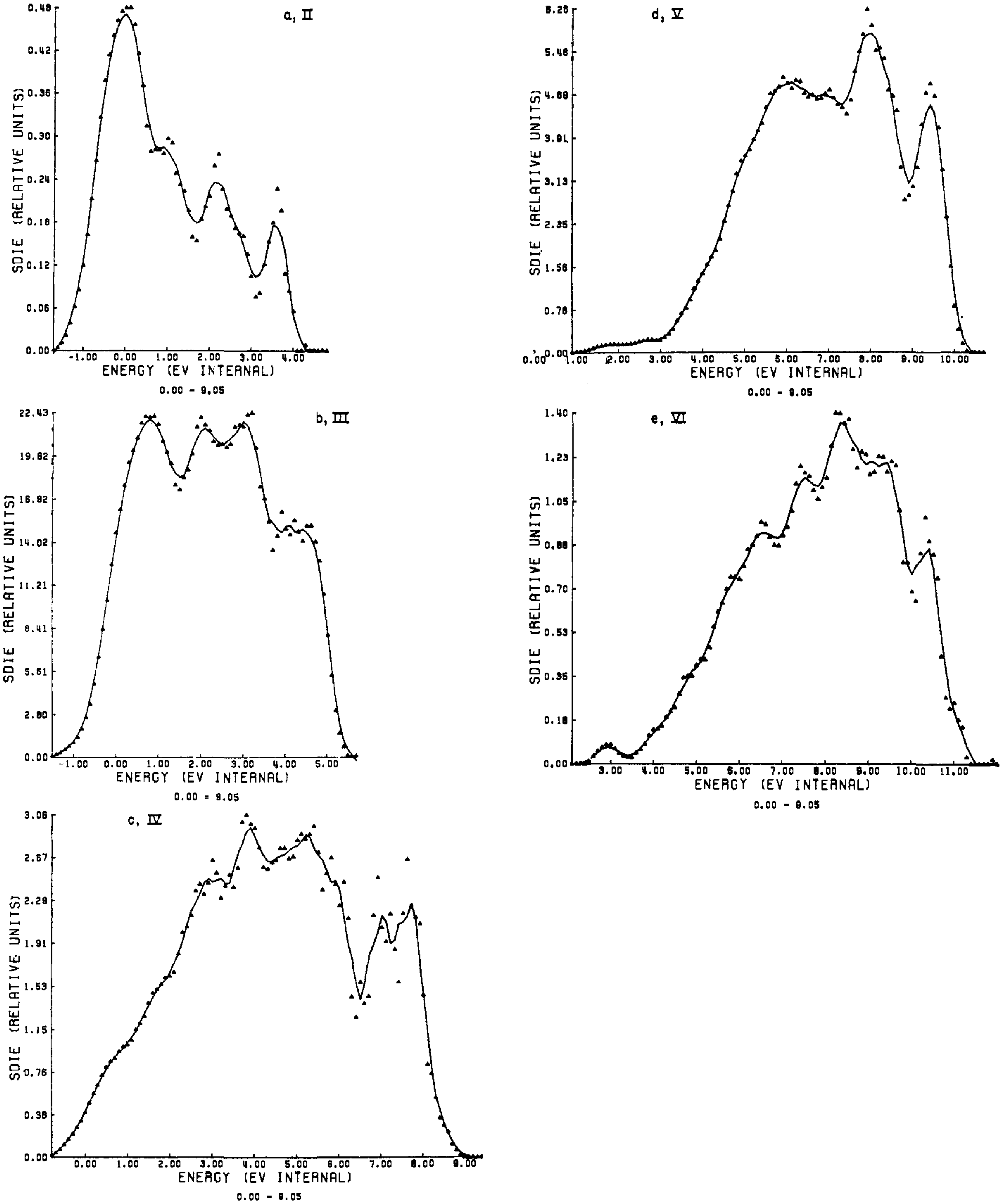


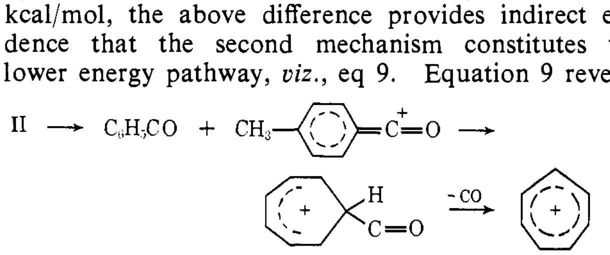
Figure 3. Plots of d^2I/dE^2 and SDIE values for II through VI *vs.* internal energy.

and two-bond mechanisms, respectively. The SDIE curve in Figure 3b and the average value of 9.84 ± 0.10 eV for the experimental appearance potential for III are thus clearly consistent with only the one-bond mechanism, *i.e.*, Scheme I. The calculated appearance potentials for formation of IV *via* Scheme I and eq 8 are 10.02 ± 0.17 and 10.86 ± 0.22 eV, respectively. Although Figure 3c indicates no well-defined appearance potential for IV, the value must for the following reasons be less than 10.86 eV and, consequently, eq 8 represents an implausible mechanism. The slow rise in the SDIE curve in Figure 3c demonstrates that the appearance potential must be lower in value than the first local miximum occurring at *ca.* 11.8 eV. In all determinations of the SDIE curve for IV, a region of inflection was observed at *ca.* 9.90 to 10.15 eV which overlaps the appearance potential calculated for the mechanism in Scheme I. The broadening in the SDIE curves is to be expected from the statistical theory.[6g]

The appropriate metastable transitions reveal that V and VI correspond at least in part to second-generation fragment ions formed by loss of CO from III and IV, respectively. Metastable ions were not detected for the direct formation of V and VI from the molecular ion.

On the assumption that the C_7H_7 ion (V) has a tropylium ion structure,[37] we calculate values of 10.37 ± 0.47 to 11.37 ± 0.52 eV for the appearance potential of V. The SDIE curve in Figure 3d exhibits a very slow rise up to an internal energy of *ca.* 3.5 eV. The experimental C_7H_7 ionization efficiency curve approaches the energy axis asymptotically; *i.e.*, the ion intensity is small but detectable up to *ca.* 11 eV and starts to increase rapidly in the region 12.5–13 eV.

While the tropylium ion structure may not be involved in all instances in which the C_7H_7 ion is a participant, we believe that our results can be best rationalized in terms of this structure by considering the energetics of CO loss from III. Two plausible mechanisms are: (1) ring expansion subsequent to CO loss, and (2) ring expansion preceding or simultaneous with expulsion of CO. Although the heat of formation (ΔH_f) of the 4-methylphenyl cation is unknown, ΔH_f for $C_6H_5^+$ is at least 50 kcal/mol in excess of the value for $C_7H_7^+$ formed by dissociative ionization of toluene.[38] Since replacement of a *p*-hydrogen in $C_6H_5^+$ by a methyl should not decrease ΔH_f by more than 15 kcal/mol, the above difference provides indirect evidence that the second mechanism constitutes the lower energy pathway, *viz.*, eq 9. Equation 9 reveals



(9)

that III must at a minimum undergo migration of two hydrogens and insertion of the exocyclic carbon into the six-membered ring. The energy required for such a rearrangement must be initially present in the molecular ion. Because of the similar number of degrees of freedom in the products, the excess energy in the molecular ion will on the average be partitioned in the first fragmentation nearly equally between the benzoyl radical and III. Hence the long tail in the *m/e* 91 ion SDIE curve is consistent with the remark by Wallenstein and Krauss[39] that there are wide statistical fluctuations about this average. A tighter activated complex is expected for a rearrangement–fragmentation reaction than for a simple dissociative process.[14] Thus *k*(*E*) for CO loss from III should exhibit an initial slow rise with increasing internal energy. Consequently, the C_7H_7 ionization efficiency curve should approach the energy axis asymptotically.

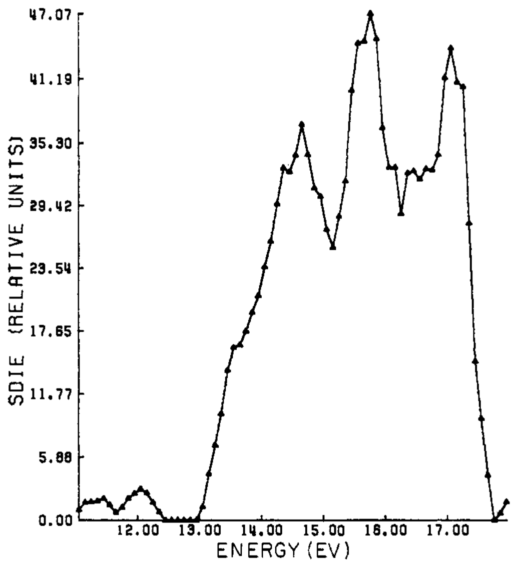


Figure 4. The SDIE curve of the metastable ion for CO loss from III.

A broad Gaussian-shaped peak was observed for the metastable ion for formation of V. Spectra recorded at 3.5 kV on the LKB 9000P and at 8 kV on the CEC-21-110B provide tenuous evidence for the presence of a flat-topped peak superimposed on the high mass side of and having only 5–10% of the intensity of the normal metastable ion peak. The metastable ion was just sufficiently intense to permit measurement of d*I*/d*E*. The resultant SDIE curve is shown in Figure 4. The rapid, and unexpected,[6g–i] decrease at high energy results from premature truncation of d*I*/d*E* required by excessive noise in the signal. As expected, the general features in the SDIE curve for the normal *m/e* 91 ion are mirrored in the SDIE curve in Figure 4.

In a review of the thermodynamics of formation of the C_6H_5 ion, Harrison[38] points out that an acylic structure may well obtain for the *m/e* 77 ion formed by loss of CO from the benzoyl ion in the mass spectra of benzaldehyde and acetophenone. Thus, by analogy, a similar structure is expected for VI. Although the appearance potential for VI is not well-defined, the SDIE curve in Figure 3e is not inconsistent with an appearance potential of 13.95 ± 0.66 eV based upon ΔH_f of the C_6H_5 ion in the mass spectra of benzaldehyde and acetophenone.

Comments on the SDIE Curve for II. The maxima at 1.00, 2.20, and 3.60 eV in the SDIE curve in Figure 3a cannot be regarded as experimental artifacts because they were observed in repeated determinations. Based upon all determinations of the SDIE curve, the values are 10.16 ± 0.11, 11.16 ± 0.12, and 12.72 ± 0.12 eV. Either autoionizing or excited ionic states long-lived with respect to internal conversion to the electronic ground state of II (otherwise one would observe fragment but not parent ions) constitute alternative explanations. The former could be reflected by the presence of maxima at the same electron energy in the SDIE curves for II, III, and IV, whereas the latter could lead to maxima in these curves at higher electron voltages, if these states in II fragment according to Scheme I. Although the SDIE curve for III in

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(37) H. M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 10.

(38) A. G. Harrison, "Topics in Organic Mass Spectrometry," Vol. 8, A. L. Burlingame, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 121–166, and references cited therein.

(39) M. B. Wallenstein and M. Krauss, *J. Chem. Phys.*, **34**, 929 (1961).

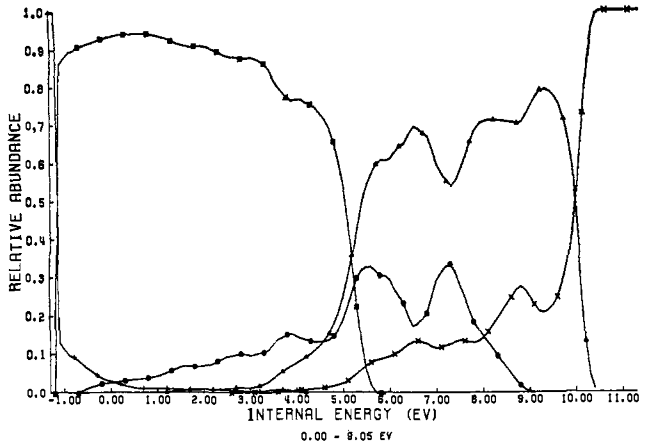

Figure 5. The breakdown graph; +, ⊡, ⊙, ▲, and × represent II through VI, respectively.

Figure 3c, and to some degree the one for IV in Figure 3d, may be construed as marginally favoring the excited state over the autoionization interpretation, no real choice between the alternative explanations is presently possible. Regardless of their origin, the probability of detecting a molecular ion in one of these states is quite low; *vide post.* It is noted that only 30% of all stable II is formed with energies in excess of 1.7 eV.

Breakdown Graph. The breakdown graph obtained from the SDIE values for each ion normalized by their sum at each value of the internal energy of the molecular ion is presented in Figure 5. For identification purposes a few points are included on each curve. The extension of the energy axis to negative values represents the effect of the electron energy distribution and probably the internal thermal energy of I. The breakdown graph exhibits features qualitatively similar to ones deduced experimentally[6i,j,9–11] and theoretically[3,6a,12] for hydrocarbons. It is clear that the probability of detecting II in states corresponding to the maxima at 1.00, 2.20, and 3.60 eV in Figure 3a is very low. Within the limits imposed by the electron energy spread, II ions possessing up to 0.1 to 0.2 eV of excitation energy are stable. A further slight increase in the internal energy produces a rapid decrease in the half-life of II and, hence, $k_1(E)$ must rise to a value of *ca.* 10^5–10^6 sec^{-1} within an internal energy interval of 0.1 eV or less.

As the internal energy of II is increased from −0.9 to 5 eV, the total yield of III, *i.e.*, III plus IV, decreases from *ca.* 94 to 80%. In this internal energy interval the probability that II will fragment to produce IV slowly rises to a value of *ca.* 0.2. Thus, the 4-methyl substituent exerts a dominant influence on the kinetics of competitive cleavage of the C1–C2 bond in molecular ions possessing up to 5.0–5.5 eV of internal energy. Figure 5 shows that deposition of energy in excess of 5.6 eV in II results in a significant increase on the average in the probability of forming IV and a diminution in that of forming III. In fact, such II accounts for 32% of all stable and 40% of all IV formed.

For internal energies of II in excess of 5.8 eV, the rate constant for the fragmentation III → IV, $k_3(E)$, is sufficiently large that no stable III is observed. To attain a correspondingly large rate constant for formation of VI from IV, *i.e.*, $k_4(E)$, requires *ca.* 9 eV of internal energy.

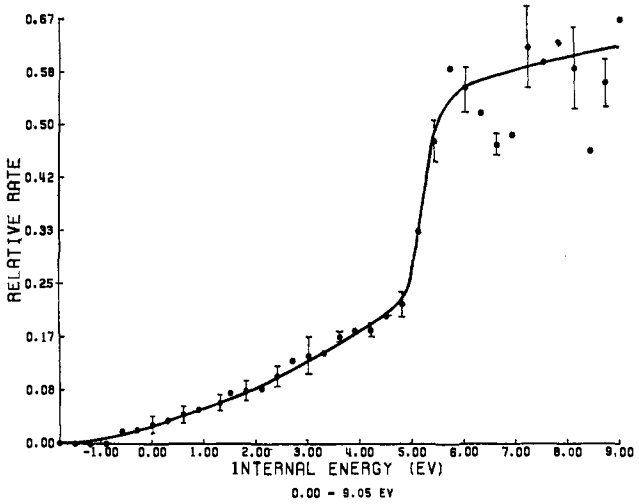

Figure 6. The ratio of rate constants for formation of IV and III as a function of internal energy.

Energy Dependence of Competitive Fragmentation Processes. The ratio of rate constants for formation of IV, $k_2(E)$, and III, $k_1(E)$, at the *i*th value of the internal energy is given by eq 10. At 0.1-eV intervals relative

$$\frac{k_2(E_i)}{k_1(E_i)} = \frac{\text{SDIE(IV)}_{E_i} + \text{SDIE(VI)}_{E_i}}{\text{SDIE(III)}_{E_i} + \text{SDIE(V)}_{E_i}} \tag{10}$$

rates were calculated for four sets of SDIE curves, and the values were then averaged. The smoothed curve drawn through these values is reproduced in Figure 6. Since the presentation is unaffected by the number of points included, average values are indicated at 0.3-eV intervals for visual clarity. Deviations are shown for points separated by 0.6 eV. In general, the average deviation in any given average relative rate is *ca.* 10 to 25% of its value.

As shown in Figure 6, the rate of formation of IV relative to the rate of formation of III was observed, within the limits of experimental precision, to increase in a smooth fashion with increasing excitation energy of II up to an internal energy of about 4.8 eV. Although complete randomization of energy cannot be achieved, if some fraction of molecular ions are produced in long-lived states,[6g,5b] *vide supra*, for II produced with less than 4.8 eV of internal energy, the variation in $k_2(E)/k_1(E)$ with energy is good evidence that either energy randomization must be essentially complete or the values of $k_2(E)$ and $k_1(E)$ for fragmentation of the excited states must approximate those for the ground state, or both.

Although the ionization potentials of the 4-methylbenzoyl radical and the benzoyl radical are apparently unavailable, Figures 5 and 6 led by Stevenson's rule[40] to the conclusion that the former has the lower value. The lower ionization potential of the 4-methylbenzyl radical[41] (7.46 eV), compared with the benzyl radical[41] (7.76 eV), constitutes evidence supporting this conclusion by analogy.

The ratio of relative rate constants is observed to

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(40) D. P. Stevenson, *Discuss. Faraday Soc.*, 10, 35 (1951).

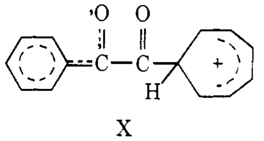
(41) A. G. Harrison, P. Kebarle, and F. P. Lossing, *J. Amer. Chem. Soc.*, 83, 777 (1961).

rise discontinuously in the interval from 4.8 to 5.6 eV. From 5.6 to 9 eV the relative rate appears to be essentially independent of the internal energy within the limits of precision. However, the second derivative technique underestimates the P(ED) function for VI (see discussion of ion intensities) and, hence, $k_2(E)/k_1(E)$ could increase by 20–30% as the internal energy is increased from 5.6 to 9 eV. This estimate is obtained after multiplication of the term SDIE(VI)$_{E_i}$ in eq 10 by the ratio of the experimental to the calculated 70-eV ion intensities for VI. Relative rates were not calculated for internal energies in excess of 9 eV because at higher energies the SDIE curves for V and VI are decreasing to zero and those for fragment ions not studied, *e.g.*, the C_5H_5 ion, have finite values.

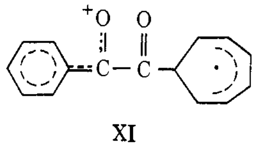
The behavior in $k_2(E)/k_1(E)$ from 5.6 to 9 eV is not reasonably ascribed to a systematic error because the rate constant ratio for competitive fragmentations of the 1-phenyl-d_5-2-phenylethane-1,2-dione molecular ion exhibits a random variation of 10–20% at corresponding internal energies.[42]

Autoionization represents a possible although somewhat implausible explanation for the behavior of the rate constant ratio for molecular ions possessing in excess of 4.8 eV of internal energy. First, the region of interest represents ionization produced by electrons possessing energy in excess of 14.6 eV. Chupka and Kaminsky[6i] have commented that for electrons of moderate to high energies autoionization should contribute only a minor amount to the total ionization. Second, if autoionization were influencing the rate constant ratio for II, a similar phenomenon would have been expected for fragmentation of the structurally analogous 1-phenyl-d_5-2-phenylethane-1,2-dione molecular ion.

Another explanation involves decomposition of II at least in part in an isolated but not long-lived electronic state(s). If the hypersurface for II at some 5 eV of internal energy intersects the surfaces of the 1-cyclohepta-2,4,6-trien-1-yl-2-phenylethane-1,2-dione molecular ions X and XI, competition occurs between ring expansion of II to form X and XI and randomization of its energy over lower-lying states. Thus at these internal energies some fraction, if not all, of primary fragmentations will occur from states corresponding to X and XI. Because of charge localization, dissociation of the C1–C2 bond in X produces only the m/e 119 ion and in XI only the m/e 105 ion with rate constants $k_1'(E)$ and $k_2'(E)$, respectively (see eq 11 and 12). In contrast to the situation in Scheme I (see also eq 9), the m/e 119 ion formed *via* eq 11 possesses a ring-expanded structure. At the energies of interest, $k_3'(E)$ is conceivably large enough that stable m/e 119 ions are not formed.

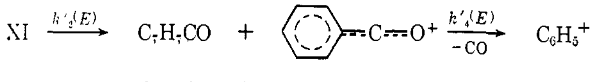


X



XI

(11)



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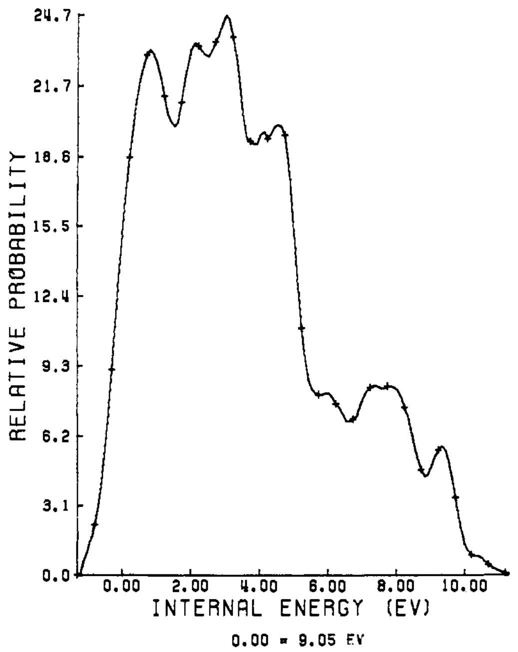

Figure 7. The energy deposition function applicable to the 70-eV mass spectrum of I.

Finally, if the discontinuity in $k_2(E)/k_1(E)$ occurring at 4.8–5.6 eV of internal energy does signify a change in mechanism, then the ratio of the intensities of IV and III in mass spectra of I produced by moderate- to high-energy electrons (20–70 eV) bears no simple relationship to the effect of a methyl group on the kinetics of dissociation of the C1–C2 bond in II.

Energy Deposition Function. The energy deposition function, P(ED), applicable to the 70-eV mass spectrum of I was obtained by summing the SDIE curves in Figure 3 and is reproduced in Figure 7. Even if the second derivative technique yielded the exact energy deposition function the P(ED) function in Figure 7 is incomplete owing to the neglect of processes occurring at ionizing energies above 19–20 eV. Interestingly, II are formed with a wider range of internal energies than are the molecular ions from propane and butane.[6i] Thus the excitation cross section for interaction of the electron beam with I must be greater than for hydrocarbons. Lack of knowledge of orbital energies for I prohibits discussing the expected general form of P(ED) as done by Chupka and Kaminsky[6i] for propane and butane. Since 26% of the area under the curve in Figure 7 occurs at internal energies in excess of 5.6 eV, high-energy molecular ions must contribute significantly to the 70-eV mass spectrum of I.

Comparison of Calculated and Experimental Ion Intensities. Table III tabulates calculated and experimental ion intensities normalized to a value of 100 for III. In accordance with the threshold law, calculation of the intensity of a given ion produced by low-energy electrons requires a double integration of the SDIE curve or equivalently the integration of the FDIE curve. For example, the ion intensities predicted for the 10-eV mass spectrum of II are based upon a Simpson's rule double integration of the SDIE curves for

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[42] S. E. Scheppele, R. K. Mitchum, and J. H. Draeger, unpublished results.

Table III. Relative Ion Intensities in the Mass Spectra of 4-Methylbenzil

	Relative intensities at					
	10 eV		15 eV		70 eV	
Ion	Calcd[a]	Exptl	Calcd	Exptl	Calcd[b]	Exptl
II	4.3	4.3	1.3[b]	1.3	1.3	1.3
III	100	100	100[a,b]	100	100	100
IV	2.8	3.2	8.1[a]	9.0	16.8	20.2
V			2.2[a]	2.7	25.8	26.3
VI			0.2[a]	0.3	5.9	15.7

[a] Based upon double integration of SDIE curves. [b] Based upon single integration of SDIE curves.

II, III, and IV through 0.95 eV of internal energy (Simpson's rule single integration of the FDIE curves through 10 eV of beam energy). As seen in Table III, good agreement is realized between the calculated and experimental intensities for 10- and 15-V electrons. Thus, the data in Figure 1 correspond essentially to the first derivative of the ionization efficiency curves.

For 70-V electrons, the agreement between the experimental ion intensities and those obtained from a single Simpson's rule integration of the SDIE functions is seen to be reasonable for all ions except VI. The low value of the predicted intensity for VI does not represent experimental error since Simpson's rule integration of FDIE up to its experimental maximum recovers the ion intensity; *i.e.*, the deviation between the experimental and the so calculated ion intensities in all instances was 10% or less. Thus, the discrepancy between the predicted and the observed intensities for VI produced by 70-V electrons is indicative of a nonlinear threshold law for formation of the *m/e* 77 ion. However, the threshold laws for formation of II through VI must at least approximate linear functions. Assuming the validity of these deductions, it follows apodictically that the second derivative technique (a) yields reasonable estimates of the *P*(ED) functions for formation of II through V and (b) underestimates the *P*(ED) function for formation of VI.

Comparison of the experimental intensities with those calculated from a single integration of SDIE reveals that 15-V electrons are sufficient to overcome the threshold laws for formation of II and III and, hence, to produce a constant yield of II relative to III.

Acknowledgments. Financial support by the Oklahoma State University Research Foundation is acknowledged. We thank the National Science Foundation for making available the LKB-9000P through Professor G. R. Waller (GB-7731) and the Robert A. Welch Foundation for financial support of that portion of the research conducted at the University of Houston. Thanks are also due Professor D. F. Hale of the Department of Mathematics at the Oklahoma State University for discussions pertinent to the numerical analysis and Professor O. C. Dermer for comments on the manuscript.

Appendix

Thermodynamic Calculation of Ionization and Appearance Potentials. The deviation associated with each of the calculated values pertinent to the mass spectrum of I was computed by the standard method.[25] For each quantity used in a given calculation, the deviation was: (a) the cited value; (b) the average deviation, if two or more estimates were available; or (c) in the absence of either a or b, assumed to be 5% of its value.

The ΔH_f of I, which to our knowledge has not been determined experimentally, was estimated as follows. The ΔH_f of VII is −21.8 kcal/mol.[43] The group equivalents[44] value for ΔH_f of 4-methylbenzaldehyde[45] (−21 kcal/mol), compared with the experimental ΔH_f of benzaldehyde[45] (−10.5 kcal/mol), and the group equivalents value for ΔH_f of 4-methylbenzophenone[45] (3.3 kcal/mol), compared with the experimental ΔH_f for benzophenone[45] (12.5 kcal/mol), yield values of −10.5 and −9.2 kcal/mol, respectively for $\Delta\Delta H_f$ for replacement of a *p*-hydrogen by methyl. Combining these values with ΔH_f(VII) gives values of −31.0 and −32.3 kcal/mol for ΔH_f(I). By the group equivalents method, ΔH_f(I) is −28.3 kcal/mol. These three values yield a arithmetic mean value of −30.54 ± 1.48 kcal/mol for ΔH_f(I).

Based upon the value 8.86 ± 0.14 eV for the ionization potential of VII and ΔH_f(VII), ΔH_f of the molecular ion of VII (XII) is calculated to be 182.5 ± 3.6 kcal/mol, which is comparable with the value of 180 kcal/mol reported previously.[26a] The $\Delta\Delta H_f$ for replacement of a *p*-hydrogen in XII by a methyl was estimated to be −14.50 ± 0.72 kcal/mol from ΔH_f of the molecular ions of 4-methylbenzophenone[45] (214 kcal/mol) compared with benzophenone[45] (228 kcal/mol) and 4-methylbenzaldehyde[45] (194 kcal/mol) compared with benzaldehyde[45] (209 kcal/mol). Thus, ΔH_f(II) is estimated to be 168.0 ± 3.7 kcal/mol. The ionization potential of I is then calculated to be 8.61 ± 0.17 eV.

Equation 13 is applicable to the formation of III *via* Scheme I.

$$\mathrm{AP(III)} = \frac{\Delta H_f(\mathrm{III}) + \Delta H_f(105) - \Delta H_f(\mathrm{I})}{23.06} \tag{13}$$

Taking a recent value of 26.1 ± 2.0 kcal/mol for ΔH_f of the benzoyl radical[46] and a value of 167.7 ± 3.2 kcal/mol for ΔH_f(III), *vide post*, leads to a value of 9.73 ± 0.18 eV for AP(III). Equation 14 is valid for formation

$$\mathrm{AP(III)} = \frac{\Delta H_f(\mathrm{III}) + \Delta H_f(\mathrm{C_6H_5}) + \Delta H_f(\mathrm{CO}) - \Delta H_f(\mathrm{I})}{23.06} \tag{14}$$

of III *via* eq 1. Values[45] of 72.0 and 26.42 kcal/mol for ΔH_f of C_6H_5 and CO lead to a value of 10.58 ± 0.23 eV for AP(III). In the absence of the requisite experimental data, ΔH_f(III), *i.e.*, 167.7 ± 3.2 kcal/mol, was calculated from ΔH_f(IV), on the assumption that $\Delta\Delta H_f$ between III and IV equals −14.5 kcal/mol, *vide supra*.

The appearance potentials for formation of IV *via* Scheme I and eq 2 were calculated using eq 15 and 16, respectively.

$$\mathrm{AP(IV)} = \frac{\Delta H_f(\mathrm{IV}) + \Delta H_f(119) - \Delta H_f(\mathrm{I})}{23.06} \tag{15}$$

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$$AP(IV) = \frac{\Delta H_f(IV) + \Delta H_f(91) + \Delta H_f(CO) - \Delta H_f(I)}{23.06} \quad (16)$$

The appearance potential of the benzoyl ion in the mass spectrum of I was found to be 9.98 ± 0.12 eV and leads to a ΔH_f(IV) of 182.2 ± 3.1 kcal/mol. These values are close to the previously reported values of 9.7 eV and 186 kcal/mol.[26a] The ΔH_f(119) was estimated to be 18.2 ± 2.0 kcal/mol from the ΔH_f of the benzoyl radical and the difference (−7.9 kcal/mol) in the heats of formation of the 4-methylbenzyl and benzyl radicals.[45] Likewise it was necessary to use the value −7.9 and ΔH_f of the C_6H_5 radical (72 kcal/mol) to estimate the heat of formation of the 4-methylphenyl radical (64.1 ± 3.6 kcal/mol). Equations 15 and 16 lead to values of 10.02 ± 0.17 and 10.86 ± 0.22 eV, respectively, for AP(IV).

The appearance potential for formation of V from II was calculated using eq 17. Values of 232 kcal/mol

$$AP(V) = \frac{\Delta H_f(V) + \Delta H_f(105) + \Delta H_f(CO) - \Delta H_f(I)}{23.06} \quad (17)$$

from the ionization–dissociation of toluene and 209 kcal/mol from the ionization of the cycloheptatrienyl radical[45] for ΔH_f(V) lead to values of 11.37 ± 0.52 and 10.37 ± 0.47 eV for AP(V).

Equation 18 is applicable to the formation of VI from

$$AP(VI) = \frac{\Delta H_f(VI) + \Delta H_f(119) + \Delta H_f(CO) - \Delta H_f(I)}{23.06} \quad (18)$$

II. A value of 299 kcal/mol is obtained for ΔH_f of the C_6H_5 ions in the mass spectra of benzaldehyde and acetophenone.[38] Thus a value of 13.95 ± 0.66 eV is calculated for the AP(VI).

Ionic Association in Low-Dielectric Media. I. Ultrasonic Absorption Studies of Nitrates in Tetrahydrofuran

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Abstract: Ultrasonic absorption studies of lithium nitrate solutions in tetrahydrofuran at 25° have been carried out. In the frequency range 10–150 MHz there is a single concentration-independent relaxation which is not found in a number of other lithium salts. A very similar effect is found in THF solutions of tetramethyl- and tetrabutylammonium nitrates. The relaxations have been attributed to a process, possibly a desolvation, characteristic of nitrate ion within an ion pair. The influence of quadrupole formation upon the observed effect is discussed.

The Eigen multistep mechanism for ionic association[1] involves either two or three steps. The first step is the diffusion-controlled approach of free ions to form a solvent-separated ion pair (outer-sphere complex). The final step in this process is the collapse of a solvent-separated pair expelling the solvent molecule and forming a contact (inner sphere complex). In a three-step mechanism there is a third process which may be due to desolvation of the anion. Three-step and two-step mechanisms have been applied to data for $MnSO_4$ in water.[2,3]

Ultrasonic absorption has been the technique most often used for the experimental investigation of the kinetics of the first step in this process. Single relaxation processes corresponding to this step have been observed in a number of cases.[4,5] Relaxations essentially due to the formation of inner sphere complexes are common in both ultrasonic and jump methods.[6] Relaxations due to anion desolvation and which are not closely coupled to other processes have never been reported previously. We believe that we have formed a process which is characteristic only of the anion and may be a desolvation.

Experimental Section

The ultrasonic instrumentation consists of a Matec Model 6000 pulse generator–receiver, Model 666 B attenuator, and Model 120 syncronizer. The ultrasonic cell was similar to one used in earlier work.[2] A Z cut quartz delay line was used as opposed to the earlier fused quartz rod. This improved the signals at higher frequency.[7] A Hewlett-Packard Model 180 oscilloscope with a Model 182OB time base and Model 1803A amplifier was used in all measurements. The instrument was checked by measuring the absorption of both water and aqueous $MnSO_4$ solutions.

Tetrahydrofuran was distilled from lithium aluminum hydride. It was found that the value of α_0/f^2, where α_0 is the sound absorption coefficient and f the frequency, was a sensitive means of detecting moisture in the solvent. Freshly opened bottles of THF gave values about 123 × 10^{-17} neper cm^{-1} sec^2 which rose to 133 × 10^{-17} neper cm^{-1} sec^2 for distilled THF. Addition of more substantial quantities of water to THF led to relaxation processes in the solvent similar to those found for water-dioxane solutions.[8]

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