was observed with sensitizers of less than 56 kcal/mol triplet energy such as benzil and biacetyl. 1-Acetonaphthone gave a very small enhanced absorption probably because it has a marginally sufficient triplet energy of 56 kcal/mol.

However, high triplet energy is not a sufficient condition for enhanced absorption as seen in Table I. All sensitizers having a fluorescence quantum yield greater than 10^{-2} (phenanthrene, triphenylene, anthracene, and pyrene) gave an emission signal regardless of their triplet energy. The unsensitized decomposition also gave an emission signal,[6] but Corning 0-54 or 0-52 filters could screen out essentially all the direct irradiation. The appreciable room-temperature fluorescence of the hydrocarbons indicates that they have a relatively large singlet yield. The aromatic hydrocarbon sensitization must involve, at least in part, singlet energy transfer. This is confirmed by the observation of fluorescence quenching of anthracene and triphenylene by BPO in the concentration range used in the nmr experiments. The Stern–Volmer quenching constants in butyl acetate for anthracene and triphenylene are 1×10^{10} l. mol^{-1} sec^{-1} and 2.4×10^{9} l. mol^{-1} sec^{-1}, respectively, *i.e.*, close to diffusion controlled. There are a number of other examples of reactions for which singlet sensitization by triphenylene,[9-13] anthracene,[11,13] phenanthrene,[12,13] and pyrene[9,11-13] is well established. Since the absorption of anthracene, triphenylene, and pyrene occurs at longer wavelengths than that of the BPO, a possible mechanism is charge-transfer complex formation between ground-state BPO and excited singlet sensitizer.[14]

When carbon tetrachloride was the solvent in the photodecomposition of BPO, chlorobenzene was the product obtained.[6] As in the case of benzene, nmr emission was observed on direct irradiation and enhanced absorption when a triplet sensitizer was used.

The reason that 2-acetonaphthone gave an enhanced absorption while equivalent concentrations of benzophenone and xanthone gave no polarization is probably related to the well-known difference in reactivity between ketones having π–π^* and those having n–π^* triplet states.[15] Ketones with n–π^* states, like benzophenone, undergo photoreductions very readily to produce radicals which may induce the decomposition of BPO. For example, in the photosensitized decomposition of BPO, differences in product ratios have been observed between 2-acetonaphthone and benzophenone.[16] Smith interpreted his results as an induced decomposition of BPO by benzophenone-derived ketyl radicals, but that ketyl radicals are not formed in the 2-acetonaphthone case.[17] It has been predicted by Kaptein that induced decomposition leads to no net polarization.[2d] To check this hypothesis the thermal decomposition of BPO was carried out in solvents which have been reported to promote induced decomposition.[18] In neither ethylene glycol monoethyl ether nor isopropyl alcohol was nmr emission observed at temperatures which normally result in strong emission, and in dioxane or ethylene glycol monoethyl ether acetate the emission was very weak.

We conclude that the polarization of benzene formed from the decomposition of BPO is directly related to the multiplicity of the excited state in the primary photodecomposition. Enhanced absorption results from the triplet-sensitized state which occurs only when three conditions are met: sufficient triplet energy, low fluorescence yield, and little photoreduction under the reaction conditions. Direct photolysis and singlet-sensitized photodecomposition result in nmr emission.[19]

Acknowledgment. We are grateful to Dr. Saul Meiboom and Mr. Richard C. Hewitt for their patience and guidance in the use of their specially modified 60-MHz nmr spectrometer, and we are indebted to Dr. Gary N. Taylor for very helpful discussions.

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(19) Note Added in Proof. R. Kaptein, J. A. den Hollander, D. Antheunis, and L. J. Oosterhoff have studied similar systems and independently reached the same conclusion. We thank these authors for a preprint of their work.

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A Study of the $C_3H_7^+$ Ion by Ion Cyclotron Resonance Spectrometry

Sir:

The possible structures of $C_3H_7^+$ are of interest not only in mass spectroscopy[1] but also in solution chemistry,[2] radiolysis,[3] and in molecular orbital calculations.[4] A number of structures can be written for this rather simple cation including *n*-propyl, isopropyl, and various protonated propenes and cyclopropanes. Despite this variety, there is compelling evidence that the $C_3H_7^+$ ions formed from various alkanes in the mass spectrometer possess a common structure.[5] More recently, appearance potential measurements of $C_3H_7^+$ from propyl radicals show that two isomeric $C_3H_7^+$ ions exist at the threshold (presumably *n*- and isopropyl).[6] However, since these appearance potentials are nonadiabatic, there is some question as to how much smaller the adiabatic value is.[6] Appearance potentials of $C_3H_7^+$ from a variety of sources yield heats of

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(1) See W. F. Haddon and F. W. McLafferty, *J. Amer. Chem. Soc.*, **90**, 4745 (1968), and references cited therein.

(2) See G. J. Karabatsos, M. Anand, D. O. Rickter, and S. Meyerson, *ibid.*, **92**, 1254 (1970), and references cited therein.

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(5) H M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions," Academic Press, New York, N. Y., 1963, p 518.

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Table I. Tandem Mass Spectrometer Results[a]

		Products				
		$C_3H_7^+$ ($2\text{-}C_3H_7I$) + furan		$C_3H_7^+$ (C_3H_8) + furan		$C_4H_4O^+$ (furan) + 2-iodopropane
		Relative abundance				
m/e	Ion	60 eV	15 eV	60 eV	15 eV	60 eV
54	C_4H_6 or C_3H_2O	0.014	0.015	0.011	0.015	
67	C_4H_3O or C_5H_7	0.48	0.47	0.45	0.43	
93	C_7H_9	0.046	0.042	0.040	0.041	
111	$C_7H_{11}O$	0.44	0.45	0.45	0.49	

[a] The ion kinetic energy was 0.3 eV. Collision chamber temperature and pressure were 175° and 5×10^{-3} Torr, respectively.

formation which cluster around the two values determined from the ionization of the *n*- and isopropyl radicals.[7] Recent radiolysis studies of various butanes show that both $CH_3CH_2CH_2^+$ and $CH_3CHCH_3^+$ are formed,[3a] and that the *n*-propyl ion rearranges to the isopropyl and protonated cyclopropane ions.[3b] However, collision-induced metastable abundances indicate a single $C_3H_7^+$ fragment formed in the electron impact of various alkanes and bromopropanes.[1] Since the $C_3H_7^+$ ion is of such interest, and since its structure is still unsettled, we have begun a study of this ion by ion cyclotron resonance spectrometry (icr).

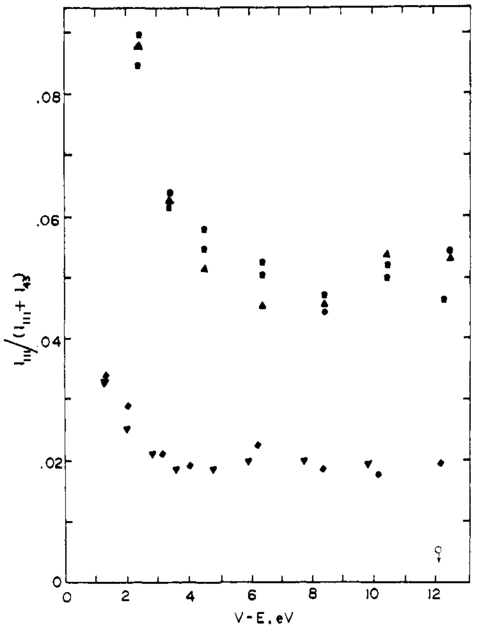

Figure 1. $I_{111}/(I_{43} + I_{111})$ *vs.* $V - E$, where V is the electron energy and E is the ionization potential; mixture, C_3H_7X-furan = 1:4. The mixtures were prepared in the icr cell by using a dual inlet system and first admitting furan. The partial pressures were obtained from the output current of the ion pump; total pressure = 5×10^{-6} Torr. The electron energy was measured by a digital voltmeter. The emission current was maintained at less than 0.2 μA for these measurements: ●, 2-iodopropane; ▲, 2-bromopropane; ■, 2-chloropropane; ▼, 1-iodopropane; ◆, 1-bromopropane; ○, 1-chloropropane.

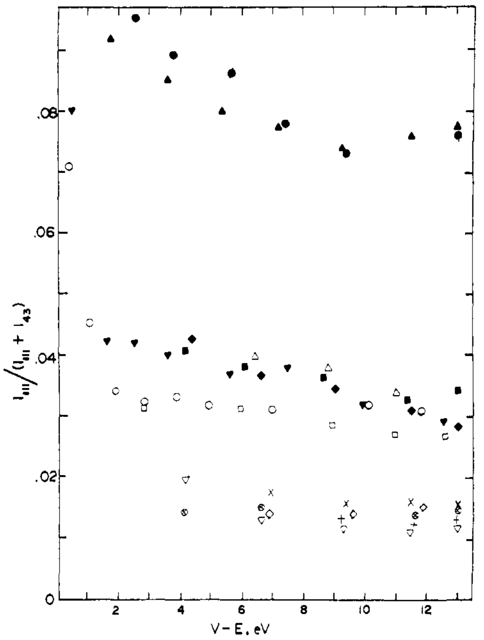

Figure 2. $I_{111}/(I_{43} + I_{111})$ *vs.* $V - E$, where V is the electron energy and E is the ionization potential: mixture, C_3H_7X-furan = 4:2; $P = 6 \times 10^{-6}$ Torr; ●, propane; ▲, 2-iodopropane; ■, 2,2-dimethylbutane; ◆, *n*-octane; ▼, 1-iodopropane; ○, 1-bromopropane; △, 2,3,4-trimethylpentane; □, *n*-heptane; ▽, 2,3-dimethylbutane; ⊗, isopentane; ◇, 1-chloropropane; ×, *n*-pentane; +, *n*-hexane.

The principles of icr have been previously discussed[8] and some applications for structure determination of gas-phase ions have been reported.[9]

When various compounds which produce abundant $C_3H_7^+$ ions upon electron impact are mixed with furan in the icr spectrometer, an abundant product ion is observed at *m/e* 111 (presumably $C_7H_{11}O^+$). Pulsed double-resonance studies[10] indicate that $C_3H_7^+$ is the primary precursor for this product *via* an exothermic reaction (a decrease in the abundance of *m/e* 111 is observed when *m/e* 43 is irradiated). However, an increase in the abundance of *m/e* 111 is observed when *m/e* 68 ($C_4H_4O^+$) is irradiated. No other ions were found to affect the abundance of this product. In order to eliminate any possible doubt that $C_3H_7^+$ is the sole precursor, mixtures of furan with 2-iodopropane or propane were investigated on a tandem mass

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(7) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS No. 26, U. S. Government Printing Office, Washington, D. C., 1969.

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(10) For a discussion of the thermodynamic implications of double-resonance studies, see J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

spectrometer.[11] It is clear from Table I that reaction 1 is the dominant means of production of $C_7H_{11}O^+$.[12]

$$C_3H_7^+ + C_4H_4O \longrightarrow C_7H_{11}O^+ \qquad (1)$$

Since the propyl ion is clearly established as the major primary ion in reaction 1, we undertook a study of this ion prepared from various sources. A study of the various 1- and 2-halopropanes is illustrated in Figure 1. Instead of finding a common reactivity for all propyl ions, the ion from 2-halopropanes is clearly more reactive than that from 1-halopropanes, and that from 1-chloropropane is even less reactive, since no product $C_7H_{11}O^+$ ion could be detected under the conditions of the study.

A second study was conducted at higher partial pressures of C_3H_7X in order to examine the whole spectrum of propyl ion reactivities (Figure 2). The propyl ions group themselves into three reactivity classes. Class I (greatest reactivity) includes the 2-halopropanes and propane, class II (intermediate reactivity) includes 1-bromo- and 1-iodopropane and various hexane, heptane, and octane isomers; and class III (lowest reactivity) includes 1-chloropropane and various pentane and hexane isomers. The reactivity of the propyl ion from propane is not surprising since it is known that a secondary hydrogen is lost in its production.[13] The reactivity exhibited by the propyl ion from isopentane and 2,3-dimethylbutane is indeed surprising, however, since *a priori* one would predict this ion to resemble those produced in class I.

In all cases, the relative abundance of the complex at *m/e* 111 increased as the ionizing energy decreased. This is not unexpected, since the complex surely possesses less vibrational excitation at lower electron energies and is, therefore, more stable. This effect has been observed in other ion–molecule reactions which presumably occur *via* an intermediate complex.[14]

To be certain that the reactivity differences observed at high ionizing energy are not due to internal energies only, measurements were made between 0.3 and 0.8 eV above the appearance potentials[15] of the propyl ions from 1- and 2-iodopropane. In both cases, the relative abundance of *m/e* 111 leveled off at *ca.* 0.5 eV above threshold, yet the ratio of the relative abundance of *m/e* 111 was identical with that found at 20 eV.[16]

A number of explanations are possible for these observations. For example, each classification could implicate a different propyl ion structure or a different mixture of structures, whose composition remains constant with electron energy. Class I and class III propyl ions could possess a unique structure, and class II ions a mixture of these structures or the structure of class III ions with lower vibrational excitation. A third explanation is based on internal energy differences only.[17] If a 1-propyl ion rearranges during or after formation to a 2-propyl ion, 16 kcal/mol of internal excitation is released[6] which would lower the overall rate of complex formation with furan. In fact, the near-threshold reactivity of the class II ion is equal to that of class I ions at $V - E$ greater than 5 eV (Figure 2), suggesting that the class II ion possesses a vibrationally excited class I (isopropyl) structure. However, this interpretation is less probable since an additional increase in the internal excitation of the class II ion (accomplished by increasing the ionizing energy) should produce essentially no change in the rate of formation of the complex (as is observed for class I at $(V - E) > 5$ eV). Instead a drastic decrease in reactivity is observed. Therefore, we feel that the results indicate that *two*, and perhaps three, propyl ions are produced in mass spectral fragmentations.[18]

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[11] This study was made with the tandem mass spectrometer at the Aerospace Research Laboratory, Wright-Patterson Air Force Base, Ohio. We are deeply indebted to Dr. Thomas O. Tiernan and his group for making these measurements.

[12] Reaction 1 may well be the gas-phase analogy of the Friedel–Crafts alkylation reaction. Studies are underway to test this possibility.

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[15] The appearance potential was arbitrarily taken to be that electron energy at which *m/e* 43 abundance was 0.05% of that at 30 eV.

[16] Unfortunately the class I propyl ions were of insufficient abundance for a similar measurement to be made.

[17] We thank Professor F. W. McLafferty and one of the referees for making this suggestion.

[18] Many of the complications in this study can be eliminated if more selective ion–molecule reactions of $C_3H_7^+$ can be found. A search for such reactions is presently underway.

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Studies on Indole Alkaloid Biosynthesis. VI.[1] The Eburnamine–Vincamine Alkaloids

Sir:

The eburnamine–vincamine group of alkaloids[2] is an interesting family which has received considerable attention from both the structural and synthetic point of view but no results are as yet available concerning the biosynthetic pathway. Structural analysis of the various members reveals that these alkaloids may be related biosynthetically to the Aspidosperma family for which a considerable body of experimental evidence is now available.[3] If this was the case some very interesting rearrangements of the fundamental indole template must prevail and these would be rather different than the ones presently considered in the other indole alkaloid areas.[3] In this regard, Wenkert[4] has put forth a postulate which considers the implication of the Aspidosperma intermediate **1** and its rearrangement *via* **2**, **3**, and **4** to the system necessary for this family as shown by the alkaloid vincamine (**5**) (Scheme

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[1] Part V: J. P. Kutney, J. F. Beck, V. R. Nelson, K. L. Stuart, and A. K. Bose, *J. Amer. Chem. Soc.*, **92**, 2174 (1970).

[2] W. I. Taylor, *Alkaloids*, **11**, 125 (1968).

[3] For a recent review and collection of references, see A. I. Scott, *Accounts Chem. Res.*, **3**, 151 (1970).

[4] E. Wenkert and B. Wickberg, *J. Amer. Chem. Soc.*, **87**, 1580 (1965).