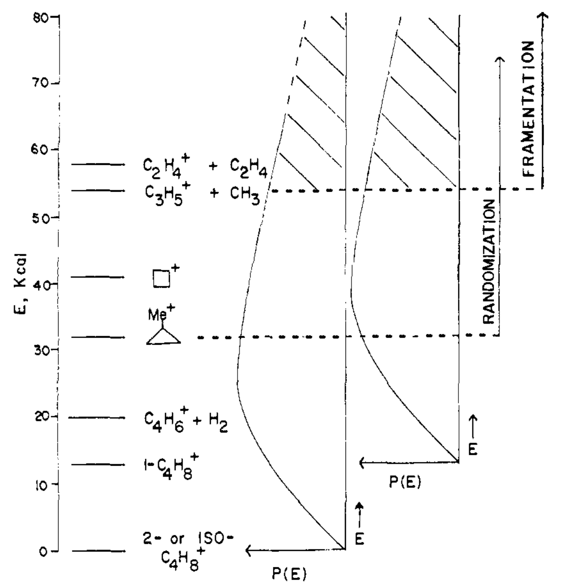

Figure 7. Schematic representation of relative energy contents of parent and fragment ions with total composition $C_4H_8^+$, with respect to the lowest energy form (butene-2 ion). Also shown are assumed energy deposition probability functions corresponding to ionization of butene-2 and butene-1 by 70-eV electrons. The shaded portion corresponds to the fraction of ions capable of yielding $C_3H_5^+$ fragments.

conveniently by considering the heats of the formations of all major species of total composition $C_4H_8^+$ (Table III). The last column lists the energy above that of the most stable structure (*trans*-2-butene ion) and reflects the minimum potential internal energy of the ion resulting from ionization of a given structure. All energy states are accessible to 70-eV electron impact, but the internal energy distribution above the ground state should vary depending on the ionization threshold. The second derivative of the total ionization efficiency curve by electron impact is thought to correspond approximately to the initial internal energy distribution of the ion,[30] and the general features of this curve do not vary greatly between similar compounds.[30,31] As a consequence cyclobutane ion will initially have a considerably higher internal energy content than the other isomers because the zero is considerably offset; it should therefore fragment considerably more. This is borne out by the 70-V mass spectra of these compounds (Table IV). The rationale is perhaps best demonstrated graphically by overlaying the estimated energy deposition distribution function of these molecules on the energy scheme, as demonstrated in Figure 7. The proportion of initial molecular ions capable of dissociation is much larger when the heat of formation of the parent ion is greater. The dissimilarities of the spectra of isobutylene and methylcyclopropane and those of the other isomers indicate that in the C_4H_8 system thermodynamic aspects dominate the fragmentation mechanism and the general features of the mass spectrum, and that the original structure enters primarily through its effect on the heat of formation of the analogous parent ion structure.

Acknowledgments. This investigation was supported in part by the United States Atomic Energy Commission and by the Robert A. Welch Foundation of Houston, Texas; we are deeply grateful for this assistance.

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Structural Effects on Electronic Relaxation Processes of Aliphatic Ketone Triplets at 77°K

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Abstract: The phosphorescence quantum yields and lifetimes of aliphatic ketones have been determined at 77°K in EPA. The results indicate that the α-CH stretching mode is a significant factor in radiationless decay, *i.e.*, $T_1 \rightsquigarrow S_0$. The phosphorescence quantum yields of the carbonyl compounds were observed to increase with alkyl substitution at the α carbon, and the phosphorescence wavelength maxima remained constant at 450 ± 3 nm. The results show that the natural radiative lifetime for phosphorescence is constant, while radiationless deactivation of the triplet is slowed down by substitution. The phosphorescence yield of di-*t*-butyl ketone in EPA at 77°K was determined to be 0.89 ± 0.10, which is greater than that of acetone by a factor of 21. Deuterated acetone exhibits enhanced phosphorescence relative to ordinary acetone. A comparison of absorption and phosphorescence data illustrates that the natural radiative lifetime for singlet and triplet are constant for the nine aliphatic ketones studied.

The photochemistry of ketones has been the subject of many investigations.[1] The lowest excited singlet of aliphatic ketones is generally accepted to be n,π^* in character and to exhibit a high intersystem crossing yield to the triplet. Data on absorption spectra have emphasized the importance of both structural and solvent effects on the n,π^* transitions of the carbonyl group.[2-5] Fluorescence studies of carbonyl

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compounds, with the exception of acetone and a few simple ketones,[2,6–13] have been given little attention. The phosphorescence quantum yield of acetone in EPA at 77°K has been reported to be 0.043.[14] Mechanisms accounting for emission properties have been proposed,[9,12,15] but radiationless decay paths have not yet been characterized.

It would be of interest to study the phosphorescence of a series of ketones for the purpose of gaining some insight concerning the factors influencing radiationless decay processes in these compounds. Aliphatic ketones are ideally suited for this type of study since the triplet yield is essentially unity in all cases. Ross, *et al.*,[16] have indicated that C–H stretching can be a significant factor in radiationless deactivation, which should be diminished by deuteration. In this investigation the phosphorescence yields and lifetimes of a series of aliphatic ketones, which may be considered as derivatives of acetone with substitution at the α carbon, have been measured.

Experimental Section

Materials. Zone-refined acetone (James Hinton, Valparaiso, Fla.) was used as received. Deuterated acetone-d_6 was obtained from Merck Sharp and Dohme, Ltd., Montreal, Canada. 2-Butanone, 3-pentanone, and 2,4-dimethyl-3-pentanone were obtained from Matheson Coleman and Bell; di-*t*-butyl ketone from K and K Laboratories, Inc., Plainview, N. Y.; and methyl cyclopentyl ketone, methyl cyclohexyl ketone, and dicyclohexyl ketone from Chemical Samples Co., Columbus, Ohio. These compounds were vacuum distilled prior to use and their purity checked with a 6 ft, $^1/_4$ in. o.d., Carbowax 20 M column on a Perkin-Elmer Model 154B gas chromatograph. Spectrograde (Matheson Coleman and Bell) EPA was used as received since emission studies indicated no interfering spectral properties.

Apparatus and Procedures. Absorption spectra were obtained with either a Bausch and Lomb Model 505 or a Beckman Model DU spectrophotometer. The natural radiative singlet lifetime, $\tau_F{}^0$, was estimated from the integrated absorption of the lowest transition of the ketone.

Phosphorescence measurements were made with a quartz dewar and an Aminco grating monochromator equipped with a rotating motor shutter assembly. The output from a 1P21 photomultiplier tube was amplified and displayed on a Moseley Model 7030A XY recorder. The emission spectra were measured at 77°K in EPA from frozen air saturated solutions. Phosphorescence lifetimes were measured with a xenon flash lamp and a Tektronix 545B oscilloscope. The phosphorescence of acetone and acetone-d_6 are unaffected by dissolved oxygen.[12,17]

All ketones were excited with 313-nm light which was isolated from an Osram 100 W/2 high pressure mercury lamp with a Schott interference filter. The monochromator entrance and exit slits were 1 mm and the emission was detected in a direction perpendicular to the exciting beam. Relative phosphorescence intensities were determined from total emission measurements in a second quartz dewar. The latter measurements eliminated the need for a lifetime correction. A planimeter was utilized to integrate the emission spectra of all solutions, which were adjusted to have the same optical densities at the wavelength of excitation.

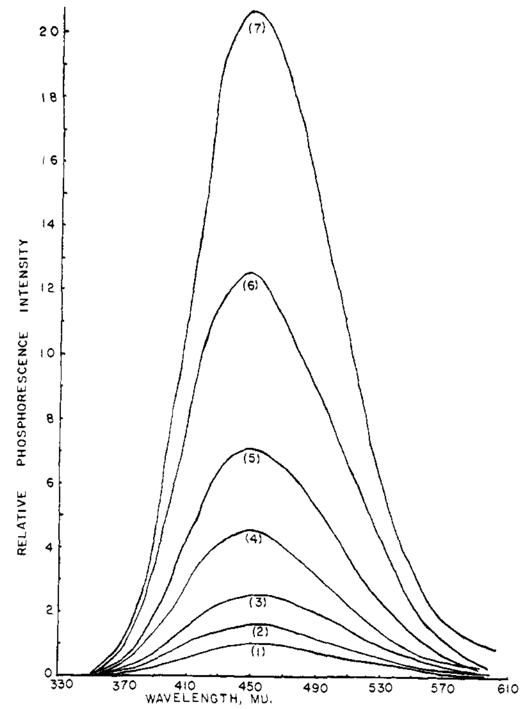

Figure 1. Phosphorescence spectra of aliphatic ketones in EPA at 77°K. (λ_{exc} = 313 nm): (1) acetone, (2) methyl cyclopentyl ketone, (3) acetone-d_6, (4) methyl cyclohexyl ketone, (5) diisopropyl ketone, (6) dicyclohexyl ketone, (7) di-*t*-butyl ketone.

Results

The most significant observation is that the phosphorescence envelopes remained constant for all the ketones studied and that the phosphorescence quantum yields increased when the α-hydrogens of acetone were replaced by various alkyl groups. It can be seen that all the phosphorescence spectra of the ketones exhibit a wavelength maximum at 450 ± 3 nm (see Figure 1). The phosphorescence yields are reported relative to acetone since its phosphorescence yield has been determined to be 0.043 in EPA,[14] and the constancy of the spectral distribution eliminates the need for correction factors associated with the photomultiplier–monochromator assembly. The results illustrate that di-*t*-butyl ketone has a phosphorescence yield of 0.89 ± 0.10, which is approximately 21 times greater than that of acetone. The total emission of the ketones was also measured at 77°K from EPA glasses, and the results paralleled the trend seen in the phosphorescence measurements, since phosphorescence is the dominant emission process.

Kearns, *et al.*,[12] observed that the phosphorescence of acetone and acetone-d_6 were identical with respect to spectral distribution, but that the intensity was 2.5 times larger for acetone-d_6. Our results, shown in Figure 1, are in agreement with their observations. They concluded that deuteration has little or no effect on the radiative triplet to ground state transition, but

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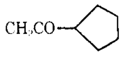
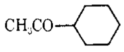
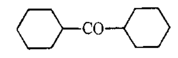
that deuteration effects phosphorescence solely through its effect on some rapid, intrinsic radiationless process.

In contrast to the trend in alkyl ketones, Richtol and Klappmeier[18] recently reported that for aliphatic α-diketones, alkyl substitution at the α carbon in biacetyl lowers the phosphorescence yield. They suggested that internal conversion of the triplet increases with increasing chain length.

Phosphorescence lifetimes of aliphatic ketones reported by McClure[19] are included in Table I, together with those measured in the present investigation. Of particular interest is the increase in the phosphorescence lifetime of the ketones with alkyl substitution at the α carbon. Using the two experimental parameters, *i.e.*, quantum yield and lifetime, the rate constants for phosphorescence, k_p, and radiationless decay of the triplet, k_{dt}, were calculated and are given in Table I. A comparison of these calculated rate constants illustrates remarkable constancy of the radiative process for the nine molecules investigated. Equally surprising is the wide variation of the rate constant for the radiationless process, which indicates that it is the determining factor for the emission intensity of these molecules. It can be seen that changes in k_{dt} parallel changes in ϕ_p and τ_p, and the correlation is quite good. These results provide convincing evidence for slowing down of radiationless decay with alkyl substitution. It is evident that the calculated rate constants in Table I include the value of unity for the triplet yield of the molecules investigated.

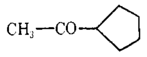
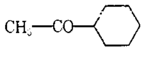
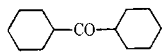
Table I. Phosphorescence Quantum Yields and Lifetimes of Aliphatic Ketones[a]

		Phosphorescence in EPA, 77°K			
		ϕ_p[b]	$\tau_p \times 10^3$, sec	k_p, sec^{-1}	k_{dt}, sec^{-1}
1.	CH_3COCH_3	0.043	0.33	77	2.9×10^3
			0.6[c]	72	1.5×10^3
2.	CD_3COCD_3	0.106			
		0.08[d]	1.0[d]	80	9.2×10^2
3.	$CH_3COC_2H_5$		0.85[c]		
4.	$C_2H_5COC_2H_5$		1.26[c]		
5.	$(CH_3)_2CHCOCH(CH_3)_2$	0.306	3.77[c]	81	1.8×10^2
6.	$(CH_3)_3CCOC(CH_3)_3$	0.89	8.6[c]	100	16
7.		0.070	0.97	72	1.0×10^3
8.		0.194	1.6	121	5.0×10^2
9.		0.54	4.3	120	1.1×10^2

[a] 313-nm excitation. [b] ϕ_p normalized to the value of 0.043 for acetone in EPA glass at 77°K (see ref 14). [c] Reference 19. [d] Reference 12.

Attempts were made to measure directly the triplet yields by triplet–triplet energy transfer in the ketone-photosensitized *cis–trans* isomerization of *cis*-piperylene.[20] This procedure, however, was complicated by irreversible photochemical processes, *e.g.*, formation of alcohol, hydrocarbon dimer, and oxetane.[21,22] There was an apparent increase in the rate of product formation with the more highly substituted ketones. The increased efficiency of the photochemical reaction between the ketone and *cis*-piperylene with increasing substitution at the α carbon is consistent with the increasing triplet lifetimes of the substituted ketones presented in Table I. The triplet yields of acetone and acetone-d_6 have each been reported to be 1.00 ± 0.10 by energy transfer studies of the acetone-photosensitized *cis–trans* isomerization of pentene-2.[17] It is reasonable to expect the triplet yields of the remaining aliphatic ketones to be unity, since all the molecules have the same natural radiative singlet lifetime (refer to Table II) and are inefficient fluorescers.

Table II. Extinction Coefficients, Wavelength Maxima, and Radiative Singlet Lifetimes for the n,π* Absorption of Aliphatic Ketones in *n*-Hexane

		ϵ_{max}	λ_{max}, nm	$\tau_F^0 \times 10^6$, sec[a]
1.	$CH_3—CO—CH_3$	14.5	279	2.5
2.	$CD_3—CO—CD_3$	14.6	282	2.5
3.	$CH_3—CO—C_2H_5$	15.8	279	2.3
4.	$C_2H_5—CO—C_2H_5$	18.6	279	1.9
5.	$(CH_3)_2CH—CO—CH(CH_3)_2$	23.0	289	1.7
6.	$(CH_3)_3C—CO—C(CH_3)_3$	20.5	298	2.0
7.		18.8	284	2.0
8.		21.9	287	1.8
9.		30.8	296	1.3

[a] τ_F^0, radiative singlet lifetime, was calculated from integrated absorption spectrum using the following expression

$$\tau_F^0 = 3.5 \times 10^8/\bar{\nu}^2_{max}\epsilon_{max}\Delta\bar{\nu}_{1/2}$$

The absorption spectra of the ketones investigated exhibit the usual solvent shift to shorter wavelengths with increasing polarity and hydrogen-bonding ability and low extinction coefficients (ϵ ~15–30), characteristic of n,π* states.[23] Relative to acetone with λ_{max} 279 nm in *n*-hexane, alkyl substitution at the α carbon produced a red shift with the lowest energy singlet being that of di-*t*-butyl ketone with λ_{max} 298 nm (see Table II). The observed wavelength maxima were in general agreement with literature values.[4,5] The extinction coefficients show a small increase with alkyl substitution as illustrated in Table II.

The natural radiative lifetimes, τ_F^0, estimated from integrated absorption spectra, are also presented in Table II. It is seen that again the radiative values for all the ketones investigated are constant.

Discussion

The invariance of the phosphorescence spectral distribution of all the carbonyl compounds investigated

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suggests that the emission process is localized in the carbonyl moiety. This explanation is consistent with molecular orbital theory, since none of the compounds studied shows conjugation with the carbonyl group. It is well known that aromatic ketones, such as acetophenone and benzophenone, do not fluoresce.[1]

From the data in Tables I and II it is seen that the natural radiative lifetimes for singlet, $\tau_F{}^0 = 1/k_F$, and triplet, $\tau_p{}^0 = \tau_p\,\phi_T/\phi_p$, are relatively constant. The slight increase for k_F with substitution is probably related to small variations of ϵ_{max}. Since the triplet yields of the ketones, on the basis of available evidence,[12,17,20,23] can be assumed to be 1.00 ± 0.10, the intersystem crossing rates are expected to be approximately 90–100 times faster than the radiative singlet–singlet transition, *e.g.*, $k_{isc} \approx 100k_F$, assuming k_{ds} is negligible. This condition is not true, however, when internal conversion of the singlet occurs. It is tempting to suggest that possibly the singlet and triplet manifold are affected in the same manner by alkyl substitution, *i.e.*, alkyl substitution at the α carbon in acetone slows down radiationless deactivation. Preliminary evidence indicates that the fluorescence yield of di-*t*-butyl ketone is greater than that for acetone.[24] A consequence of this interpretation is that there is a small amount of singlet deactivation in acetone ($\phi_{ds} \sim 0.03$), which is increasingly removed by modifying the molecule by alkyl substitution. The results for the phosphorescence in Table I confirm this effect in the triplet manifold.

In view of the above results, it is tempting to explain the increasing quantum yields associated with alkyl substitution in terms of the energies of the vibrational quanta of the C–H stretch (2900–3000 cm^{-1}), the C–D stretch ($\sim$2200 cm^{-1}), and the C–C stretch (600–1500 cm^{-1}).[25] In acetone, energy dissipation can occur *via* the C–H stretch. Since the C–C stretch involves a smaller quantum of energy than the C–H stretch, it is reasonable to expect that the probability of radiative emission would be increased upon systematic replacement of the α hydrogens with alkyl groups. The phosphorescence data for the series of ketones in Table I are consistent with this interpretation. Our observations of a deuterium effect on the emission properties with acetone-d_6 (see Table I) further corroborate this interpretation.

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Studies of Conjugated Ring Hydrocarbons: the Structure of Dimethylfulvene

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Abstract: Dimethylfulvene is one of a group of nonbenzoid conjugated ring hydrocarbons under investigation in this laboratory by electron diffraction. The intensity patterns produced by $C_5H_4CMe_2$ vapor were analyzed on the basis of a model with C_{2v} symmetry, wherein a range of bond lengths and angles was tested in a variety of plausible combinations. A least-squares analysis was applied to the experimental molecular intensity curve, and this led to the following geometrical parameters: $C_1—C_2 = 1.476 \pm 0.008$, $C_2{=}C_3 = 1.340 \pm 0.006$, $C_3—C_4 = 1.462 \pm 0.009$, $C_1{=}C_6 = 1.347 \pm 0.010$, $C_6—C_7 = 1.510 \pm 0.010$, and $(C—H)_{av} = 1.100 \pm 0.010$ Å; $\angle C_4C_3C_2 = 109.0 \pm 1.2$, $\angle C_1C_6C_7 = 122 \pm 2$, $\angle C_4C_3H_{10} = 131 \pm 2$, and $\angle C_6C_7H = 108 \pm 2°$. The methyl groups have C_{3v} symmetry with reference to the C_7–C_6 axis, apparently in a slightly distorted eclipsed conformation. Planar carbon skeleton models with uncoupled free rotation of the methyl groups and with staggered conformations were tested. None of these fit the reduced experimental molecular intensity curve better than the model with the methyl groups eclipsed.

Because fulvene is one of the isomers of benzene with three conjugated double bonds, its chemical and physical properties have been scrutinized for evidence of aromatic character. In this regard, a precision determination of its molecular geometry would probably support the chemical evidence that bonding in the fulvene framework is best described as a superposition of three butadiene-type structures. An early electron diffraction study[2] is not sufficiently conclusive, nor is the microwave analysis[3] of a single isotopic species, although the latter does prove that the molecule is planar. In the following report on the structure of dimethylfulvene the coplanarity of the carbon skeleton is again confirmed, as is the similarity of its interatomic distances to those present in butadiene. A comprehensive review of the chemistry of the fulvenes has been published recently;[4] less current are spectroscopic studies in the uv[5a] and ir[5b] and dipole moment calculations.[6]

Experimental Section

The dimethylfulvene used in this investigation was prepared by Mr. H. Banks of the Department of Chemistry, Cornell University,

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