ments.[3] Of note is that the reactivity order reported here for olefin addition is not the same as the reactivity order found for metalation of triphenylmethane.[24] This will be discussed in forthcoming publication.

In a recent study of rearrangements of certain organolithium species, evidence that the mechanism involves intermediate formation of a molecule of DPE and addition of a new organolithium species was presented.[25] Combining some direct addition studies with those on rearrangement, the authors concluded the reactivity of organolithium compounds toward DPE increases along the series phenyl < *n*-butyl < benzyl. This emphasizes the importance of the dependence of relative reactivity on reagent concentration. The concentrations we estimate for *n*-butyllithium and benzyllithium in the above studies are ~0.14 and 0.09 *F*. Figure 2 shows that this is the critical concentration where the relative reactivities of *n*-butyllithium and benzyllithium change. Considering the effect of concentration, the reactivity order derived from the above study is in accord with that indicated by these kinetic studies.

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Molecular Structure and Photochemical Reactivity. X. Aliphatic Hydroxy Ketones

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Abstract: Irradiation of an α-hydroxy aliphatic ketone, 3-hydroxy-2-butanone (acetoin), at 3130 Å yields acetaldehyde with the same quantum yield, $\Phi = 0.3$, in both gas-phase and liquid solutions. The vapor-phase quantum yield of acetaldehyde is not significantly affected by changes in temperature, but large, temperature-dependent and equal yields of CO and CH_4 were observed along with minor yields of ethanol and biacetyl. A large, solvent-dependent yield of ethanol was noted in the liquid phase. These and other products are found in 3 MeV γ irradiated samples of neat acetoin and acetoin in benzene solution. Results are interpreted on the basis of two primary photochemical reactions: (1) an intramolecular rearrangement of an excited acetoin molecule to form two molecules of acetaldehyde and (2) dissociative processes giving radicals which further react in a sequence of secondary reactions. Irradiation of neat and benzene solutions of a β-hydroxy aliphatic ketone, 1-hydroxy-2-methyl-3-butanone, with $\lambda > 3000$ Å radiation yields acetaldehyde, 2-butanone, *n*-propyl alcohol, allyl alcohol, and biacetyl. The major product of photolysis at 3130 Å and 25° in toluene solution was 2-butanone, $\Phi = 0.05$. With the exception of *n*-propyl alcohol, $\Phi = 0.026$, the quantum yields of the other products were less than 0.01 under these conditions. γ irradiation gives these products plus additional ones. Results of ultraviolet absorption and phosphorescence emission spectroscopy indicate that both hydroxy ketones have n,π^* excited singlet and lowest lying triplet states. In at least one of these, the β-hydroxy compound, the triplet state does not appear to be photochemically important.

The Norrish Type II process, an intramolecular photoelimination of an olefin from aldehydes and ketones, is a mode of decomposition common to carbonyl compounds having hydrogen atoms at the γ position of the alkyl chain.[2,3] The fragmentation occurs in both the liquid and gas phase, is generally not strongly temperature dependent, and involves an internal hydrogen atom abstraction by the carbonyl chromophore *via* a cyclic transition state.[4-7] Both singlet and triplet n,π^* states are important in this process.[8]

A notable exception to this "typical" photochemical behavior was observed in the liquid-phase photolysis of *o*-hydroxybutyrophenone at 3130 Å.[9,10] No Type II cleavage could be observed for this compound in several solvents, whereas the unsubstituted butyrophenone has a quantum yield of 0.42 for this process in both the gas and liquid phase. This quenching effect of the hydroxyl group on the Type II process is ascribed to stabilization by an internal photoenolization analogous to that earlier proposed to explain the stability toward intermolecular photoreduction shown by *o*-hydroxy and *o*-alkyl derivatives of aromatic ketones.[11,12] That such a photo-

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[1] (a) Author to whom inquiries may be addressed at the Oregon Graduate Center for Study and Research, Portland, Ore. 97225.

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[5] W. Davis, Jr., and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **69**, 2153 (1947).

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enolization actually occurs was clearly demonstrated by Yang and Rivas.[13]

In view of this intramolecular effect of hydroxyl groups on the photoreactivity of aromatic ketones, an investigation of saturated aliphatic hydroxy ketones has been initiated in our laboratory. This paper presents the results of ultraviolet irradiation at 3130 Å of an α-hydroxy ketone, 3-hydroxy-2-butanone (acetoin), and a β-hydroxy ketone, 1-hydroxy-2-methyl-3-butanone, in both the gas and the liquid phase.

Experimental Section

Gas-phase photolyses were carried out in a cylindrical quartz cell 2.5 cm in diameter and 20 cm long. The light source, a Hanovia Type 73A medium pressure mercury arc, was enclosed in a water-cooled housing and operated at 2.8 A and 165 V. The reaction cell was enclosed in an aluminum block furnace which could be heated to 300°, and the temperature was controlled to ±1% by a Brown automatic potentiometer.

The inlet manifold of the high-vacuum system, related traps, and a Bourdon pressure gauge were enclosed in a thermostated transite box which could be heated to 100°. The analytical section of the vacuum system consisted of a small downdraft mercury diffusion pump, a gas buret, and two Toepler pumps connected in series. Volatile products could be measured in the buret and transferred to a collection bulb which was subsequently attached to a mass spectrometer, gas chromatograph, or infrared spectrophotometer for analysis. The condensable products were collected inside the heated portion of the vacuum system and analyzed by the same techniques as above.

Liquid-phase photolyses were carried out in a cylindrical quartz cell having an internal diameter of 2.5 cm and a length of 0.5 cm. The light source was a PEK Labs, Inc., 110 super high pressure mercury arc filtered with 5 cm of water and a 3130 Å Jena UV-IL interference filter. Spectral purity of the light transmitted by this arrangement was verified with a modified Cary 14 spectrophotometer. Lamp intensities were measured by the method of Parker and Hatchard[14] which was modified to incorporate the use of ammonium fluoride.[10]

All ketone solutions were vacuum degassed prior to irradiation. Gas chromatographic techniques were used for the purification of the starting ketones and the identification and quantitative analysis of the reaction products. The columns employed were a 3 ft × 1/8 in. Porapak Q column, run at 118°, and a 15 ft × 1/4 in. Carbowax 20M, 20% by weight on 60–80 Chromosorb W column, run at 130°.

Ultraviolet absorption spectra were recorded on a Cary Model 14 spectrophotometer. Phosphorescence spectra were obtained with equipment constructed in these laboratories. Infrared and nmr spectra were obtained with a Perkin-Elmer Model 621 spectrophotometer and a Varian A-60 spectrometer, respectively.

Experimental Results

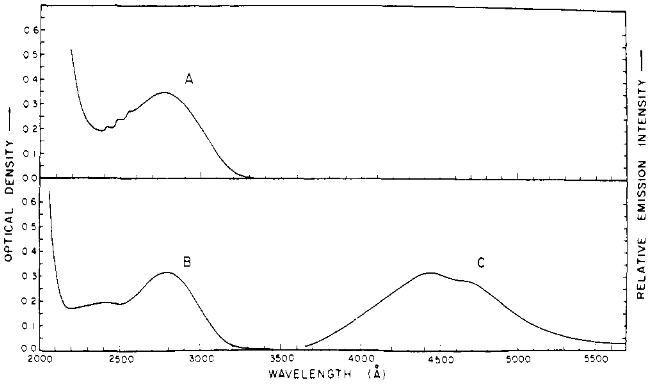

Figure 1. Absorption and emission spectra of 1-hydroxy-2-methyl-3-butanone: A, absorption in cyclohexane (1.06×10^{-2} *M*) solution; B, absorption in 4:1 ethanol-methanol (1.05×10^{-2} *M*) solution; C, phosphorescence emission in 4:1 ethanol-methanol glass at −190°. Extinction coefficients for A and B are 32.3 and 29.5 l. mol^{-1} cm^{-1} at 2800 Å, respectively, and 4.29 and 7.55 l. mol^{-1} cm^{-1} at 3130 Å, respectively. Emission is plotted with an arbitrary intensity scale.

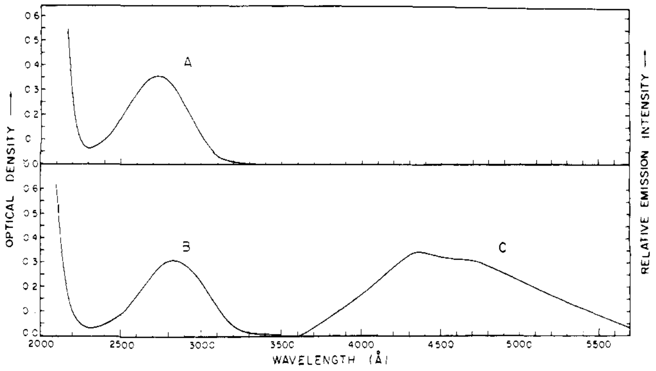

Figure 2. Absorption and emission spectra of acetoin: A, absorption in cyclohexane (1.22×10^{-2} *M*) solution; B, absorption in 4:1 ethanol-methanol (1.25×10^{-2} *M*) solution; C, phosphorescence emission in 4:1 ethanol-methanol glass at −190°. Extinction coefficients for A are 28.7 and 1.22 l. mol^{-1} cm^{-1} at 2750 and 3130 Å, respectively, and for B are 23.6 and 6.08 l. mol^{-1} cm^{-1} at 2820 and 3130 Å, respectively. Emission is plotted with an arbitrary intensity scale.

The ultraviolet absorption spectra of 1-hydroxy-2-methyl-3-butanone and acetoin in the region between 230 and 340 mμ are shown in Figures 1 and 2, respectively. In cyclohexane solution both exhibit a weak absorption band in the region 275–280 mμ. The absorption band of 1-hydroxy-2-methyl-3-butanone shifts to the blue in polar solvents as is characteristic of an $n \rightarrow \pi^*$ carbonyl transition. The absorption band of acetoin shifts to the *red* in polar solvents.[15]

The quantum yields of the major products, acetaldehyde, methane, and carbon monoxide, formed in the vapor-phase photolysis of acetoin over the temperature range of 60–150° are listed in Table I along with the pertinent experimental variables. Quantum yields of the minor products, ethanol, biacetyl, and ethane, were not measured quantitatively but are much less than Φ_{CH_3CHO} even at the highest temperatures. Variation of ketone pressure by a factor of 4 (12–49 mm) in runs 3 and 8 at 90° and change in the photolysis time by a factor of 3 has no significant effect on the quantum yields of the major products. The absorbed light intensity, I_a, was not constant throughout the series of runs but did not vary by more than a factor of 2. As seen from the results of runs 1, 2, and 11 at 120°, this much variation in I_a does not affect the quantum yields. Conversion of substrate to products was always carried out to less than 5%.

Irradiation of 0.1 *M* solutions of acetoin in *p*-dioxane and in toluene at 25° gives two major products, acetaldehyde and ethanol. Their quantum yields are 0.25 and 0.17, respectively, in both solvents. Irradiation of acetoin in acetonitrile, from which hydrogen atoms are not as easily abstracted, resulted in a significant reduction

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Table I. Vapor-Phase Quantum Yields of Major Products from Acetoin Photolysis at 3130 Å

Run	T, °C	P,[a] mm	Fract. light absorbed	I_a[b] (quanta abs/ml sec) $\times 10^{-12}$	Time, sec $\times 10^{-3}$	Quantum yields, Φ		
						CO	CH_4	CH_3CHO
1	60	61	0.330	7.33	4.65	0.17	0.19	0.35
2	60	47	0.265	7.82	3.90	0.20	0.18	0.38
3	60	46	0.260	7.67	3.89	0.20	0.18	0.40
4	80	49	0.260	11.8	2.69	0.54	0.56	0.34
5	80	12	0.069	3.07	4.35	0.58	0.52	0.30
6	90	21	0.119	5.30	3.52	0.75	0.72	0.34
7	90	22	0.123	5.48	4.01	0.75	0.72	0.33
8	120	48	0.224	11.1	2.67	1.09	1.07	...
9	120	58	0.277	13.7	1.09	1.06	1.07	0.37
10	120	54	0.260	8.02	2.93	1.06	1.07	0.35
11	150	68	0.293	9.04	2.76	1.14	1.13	0.35
12	150	61	0.273	7.31	2.44	1.12	1.12	...
13	150	72	0.311	8.33	3.66	1.16	1.15	0.35

[a] Calculated from percentage 3130-Å light transmitted through the cell employing an extinction coefficient for acetoin of 3.0.[14] [b] Based on cell dimensions of 96.3 ml.

in the quantum yield of ethanol ($\Phi_{CH_3CH_2OH} \simeq 0.06$) but not of acetaldehyde. In these experiments small amounts of biacetyl were always present as an impurity at a concentration of about 10^{-3} to 10^{-4} M; therefore, formation of this compound during photolysis was not monitored.

Neat 1-hydroxy-2-methyl-3-butanone was irradiated at 25° with light from the PEK 110 lamp filtered only with Pyrex and water ($\lambda > 3000$ Å). The products identifiable by glpc retention time were acetaldehyde, propionaldehyde, allyl alcohol, biacetyl, *n*-propyl alcohol, and 2-butanone. Irradiation of degassed solutions of 1-hydroxy-2-methyl-3-butanone in toluene at 25° and 3130 Å resulted in the formation of 2-butanone, $\Phi = 0.051$, *n*-propyl alcohol, $\Phi = 0.026$, propionaldehyde, $\Phi = 0.0074$, and acetaldehyde, $\Phi = 0.0073$. Irradiation of air-saturated solutions did not result in a significant decrease of these yields.

Preliminary gas-phase photolyses of 1-hydroxy-2-methyl-3-butanone at 170° (44 mm) were carried out with 3130-Å radiation. Product analysis is complicated by polymer formation during irradiation (also noted in solution photolysis) which might be expected if formaldehyde is formed. Due to the low conversion yields employed in these experiments (1%), products other than methane, CO, and those listed above were not detected and were not quantitatively measured. Average values for the quantum yields of carbon monoxide and methane are 0.23 ± 0.01 and 0.055 ± 0.005, respectively.

Irradiation of acetoin and 1-hydroxy-2-methyl-3-butanone (neat and in benzene solution) with 3 MeV γ rays from a cobalt-60 source resulted in the formation of the same products observed for uv-irradiated samples. Radiation yields (G values) were not obtained.

Analysis of the nmr spectra of acetoin and 1-hydroxy-2-methyl-3-butanone in carbon tetrachloride and acetone-d_6 shows no evidence of other than ketonic forms of both ketones. The hydroxyl resonance bands are found at −365 and −360 cps relative to tetramethylsilane for acetoin and 1-hydroxy-2-methyl-3-butanone, respectively. They are broad, indicating rapid intra- or intermolecular exchange. The integrated intensities and positions of resonance bands indicated no significant concentration of dimer or enol in the acetoin samples employed to obtain the ultraviolet absorption spectrum.

The infrared spectrum of acetoin exhibits a strong characteristic *intra*molecularly n-bonded hydroxyl stretching band at 3496 cm^{-1} (band width about 100 cm^{-1}).[16] We find that this band does not shift on dilution in carbon tetrachloride and persists in the infrared spectrum of acetoin vapor over a wide range of temperature and pressure. The hydroxyl stretching region in the infrared spectrum of 1-hydroxy-2-methyl-3-butanone is more complex; a strong π-bonded hydroxyl stretching band at 3601 cm^{-1} accompanies a weak n-bonded hydroxyl stretching band at 3548 cm^{-1}.[16] In addition, we find a broad band characteristic of *inter*molecular hydrogen bonding between 3000 and 3700 cm^{-1} (maximum at about 3430 cm^{-1}) which diminishes in the vapor at 80°.

The infrared and nmr spectra, while providing little information concerning the anomalous solvent shift and intensity dependences of the acetoin near-ultraviolet absorption band, do indicate that acetoin is *intra*molecularly hydrogen bonded in the liquid and the vapor. Due to *inter*molecular hydrogen bonding in 1-hydroxy-2-methyl-3-butanone and the complexity of its infrared spectrum in the hydroxyl stretching region, we did not attempt to estimate the extent of *intra*molecular hydrogen bonding of this compound.

In addition to fluorescence ($\phi_{Fl} < 0.01$), both compounds exhibit a broad, weak phosphorescence band between 375 and 550 mμ (maximum intensity at about 440 mμ) when irradiated in a 4:1 ethanol–methanol glass at −190° with light of wavelength 2537 or 3130 Å (see Figures 1 and 2). The band is structureless and short-lived in both cases (lifetime of the order of 10^{-3} sec and quantum yield, $\Phi_{Ph} < 0.03$, by comparison with acetone[17]). Similar results have been obtained with acetone, methyl ethyl ketone, and diethyl ketone.[17-19] The phosphorescent emission arises from the triplet n,π^* state in acetone.[20]

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(17) R. F. Borkman, Ph.D. Dissertation, University of California, Riverside, Calif., 1966; R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

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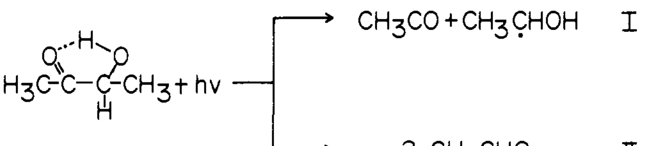
Discussion

Due to the lack of vibrational structure in the absorption and emission spectra, excited state energy levels and singlet–triplet splitting energies cannot be calculated accurately. It would appear, from examination of the spectra in Figures 1 and 2, that the 0–0 singlet–singlet and 0–0 singlet–triplet transitions take place at about 340 and 360 mμ, respectively, for both compounds. This leads to a typical carbonyl n,π* singlet–triplet splitting value of the order of 2000 cm^{-1}. The phosphorescent lifetimes and ultraviolet absorption band intensities are also characteristic of n,π* transitions for both compounds. On this basis, the first excited singlet and lowest lying triplet of both compounds are assigned as n,π* states. Several explanations for the *red* shift of the n,π* absorption band of acetoin are possible; however, no information was obtained which would permit elaboration on this point.

Primary processes I and II are proposed to explain the major aspects of the vapor-phase decomposition of acetoin when irradiated at 3130 Å. The quantum yields of the major products are shown as a function of temperature in Figure 3.



It is not known which excited electronic state(s) give rise to processes I and II; however, with regard to process II, the general hydrogen atom abstracting ability of n,π* singlet and triplet states has been established,[3,8] as mentioned above. Also, our results with air-saturated solutions strongly favors reaction from a singlet state.

Reaction II seems to be the most important primary decomposition pathway of acetoin under the experimental conditions employed. However, the primary radical cleavage, I, may also be significant since $\Phi_{\mathrm{CO}} = 0.2$ at 60° where radical decomposition and abstraction reactions are not favored. Photolyses carried out with the vapor-phase apparatus at lower temperatures (40°) were complicated by condensate formation on the reaction cell windows; reference to liquid-phase data indicates that photolysis occurred predominantly in the condensate. The liquid-phase quantum yield of CO (0.015) and CH_3CHO (0.3) formation are in agreement with yields expected from free-radical and intramolecular reaction in the liquid phase.

The major evidence for process II is the constant quantum yield of acetaldehyde over a wide temperature range and the large and equal yield of acetaldehyde in liquid-phase irradiations. Intramolecular photoprocesses are known to be reasonably temperature independent[3,5,10,21] and are not expected to be sensitive to a change in phase from vapor to liquid in contrast with free-radical processes which are inhibited due to the cage effect. This has been borne out in the case of aliphatic and aromatic ketones which undergo the Type II reaction.[3,9,10]

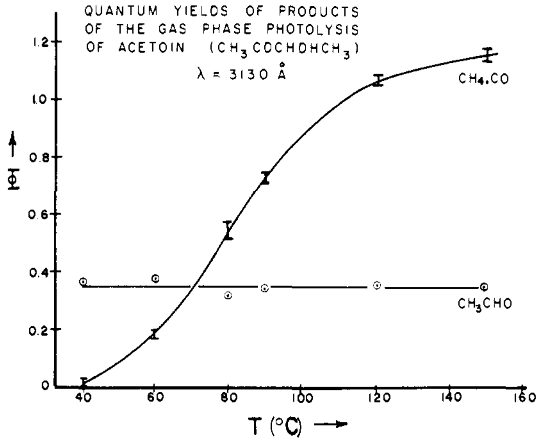


Figure 3. Quantum yields of acetaldehyde, methane, and carbon monoxide *vs.* temperature for the vapor-phase photolysis of acetoin.

If an analogy with the Norrish Type II process is valid, that is, a transfer of a β-hydrogen atom rather than a γ-hydrogen atom, reaction II probably involves internal abstraction of the hydroxyl hydrogen by the oxygen atom of the electronically excited carbonyl chromophore through a five-membered cyclic transition state. It is significant that the ground state of acetoin exists predominantly in the hydrogen bonded structure; K_{eq} for the ratio of the hydrogen bonded to the *open* structure at 25° is 25.[15] The infrared absorption results indicate that this persists in the vapor to at least 130°. Thus it seems reasonable that other possible four- and five-membered cyclic transition states do not participate to any significant extent in the formation of acetaldehyde.

This mechanism has also been suggested to account for the formation of acetaldehyde and propylene in the radiolysis of 2-pentanone[22] and is often referred to as the Type III process. It was considered with regard to the photolysis of methyl isopropyl ketone at 2537 Å in order to explain the formation of acetaldehyde and propylene,[23] but recent reports indicate that this process is not a major decomposition pathway in the case of methyl isopropyl ketone.[24]

Since substitution of the hydroxyl group at the *ortho* position in butyrophenone completely quenches the Type II elimination (which unsubstituted butyrophenone readily undergoes [$\Phi_{C_2H_4} \simeq 0.4$] in both the vapor and liquid phase), and since other ketones capable of forming internal hydrogen bonds generally undergo a photoenolization reaction, it is interesting that acetoin readily decomposes in a temperature independent process. Photoenolization of acetoin is *not* possible in the same way as it is in the case of *o*-hydroxybutyrophenone; nevertheless, reaction leading to starting material or photoinduced exchange of the carbonyl and carbinol sites may result from several plausible mechanisms. For instance, abstraction of the C_α–H hydrogen atom could lead to the formation of an ene–diol which may further react to produce acetoin. This parallels a well-known ground-state process involving ionic intermediates. One might

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[21] R. P. Borkowski and P. Ausloos, *J. Phys. Chem.*, **65**, 2257 (1961).

[22] J. N. Pitts, Jr., and A. D. Osborne, *J. Am. Chem. Soc.*, **83**, 3011 (1961).

[23] W. A. Noyes, Jr., private communication; A. Zahra, Doctoral Dissertation, University of Rochester, June 1964.

[24] W. A. Noyes, Jr., and D. Roscher, private communication.

expect process II to involve reversible or partially reversible steps such as "stretching" of the $C_\alpha O$–H bond or reverse donation of hydrogen in a biradical intermediate. These pathways for dissipation of excitation energy are not of dominant importance due to the large quantum yield obtained for acetoin decomposition, yet they may contribute significantly to the nonradiative processes which deactivate excited acetoin molecules.

Further evidence consistent with the formation of acetaldehyde in a rearrangement process was obtained from the mass spectrum of acetoin. Correlations have been observed between the modes of degradation of ketones under the influence of ultraviolet irradiation and under electron impact.[25-29] Thus, methyl ketones which undergo a photochemical intramolecular rearrangement to yield acetone and an olefin (aliphatic ketones with γ-hydrogen atoms) also show significant rearrangement peaks at *m/e* 58 in their mass spectrometric cracking patterns. The analogous rearrangement peak for acetoin occurs at *m/e* 44, CH_3CHO^+. Clearly this ion cannot be formed by any simple bond cleavage of the parent molecule.

The results of γ irradiation of acetoin (and 1-hydroxy-2-methyl-3-butanone) indicate that the reaction paths which occur are quantitatively similar for several modes of excitation since identical products are found from ultraviolet and γ irradiation and electron impact.

Primary Process I and Secondary Reactions

Of the various possibilities for the formation of radicals, reaction I is most probable based on the known behavior of the acetyl radical[30] and the formation of biacetyl at low temperatures (less than 100°). Pinacol, which might be expected from dimerization of the accompanying radical formed in I, was not observed as a product in either the liquid- or gas-phase studies. This may be due to the difficulty inherent in pinacol detection *or* to a faster rate for reaction 1 than for the dimerization process. Relatively high substrate concentrations and the lability of the tertiary hydrogen atom tend to favor reaction 1. The activation energy for the recombination process is probably near zero but its rate depends on the square of the low concentration of the methylhydroxymethyl radical. Thus, it appears reasonable for reaction 1 to compete effectively with pinacol formation in both the solution and gas-phase photolysis of acetoin.

Secondary Reactions

$$CH_3\underset{\cdot}{C}HOH + CH_3COCH(OH)CH_3 \rightarrow CH_3CH_2OH + CH_3CO\underset{\cdot}{C}(OH)CH_3 \quad (1)$$

$$CH_3CO\underset{\cdot}{C}(OH)CH_3 \rightarrow CH_4 + CO + CH_3\underset{\cdot}{C}O \quad (2)$$

$$CH_3\underset{\cdot}{C}O \rightarrow CH_3\cdot + CO \quad (3)$$

$$CH_3\cdot + CH_3COCH(OH)CH_3 \rightarrow CH_4 + CH_3CO\underset{\cdot}{C}(OH)CH_3 \quad (4)$$

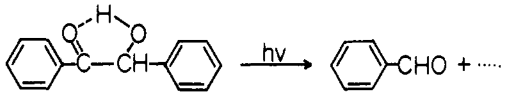
$$2CH_3\cdot \rightarrow C_2H_6 \quad (5)$$

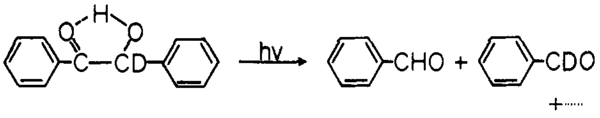
$$2CH_3\underset{\cdot}{C}O \rightarrow CH_3COCOCH_3 \quad (6)$$

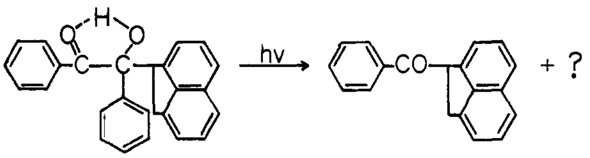
The secondary thermal reactions 1–6 are those which appear most plausible and consistent with the products and their quantum yield variation with temperature. Quantum yields for the formation of carbon monoxide and methane, Φ_{CO} and Φ_{CH_4}, are equal within experimental error and increase with temperature to a value of 1.2 at 150° (see Figure 2), indicating the presence of a chain process in the system initiated by the radicals formed in I.

The dimerization and abstraction reactions are not unusual in any respect; thermal reactions of the methyl and acetyl radicals have been studied in detail by many investigators.[3,31] Abstraction by radicals at the tertiary hydrogen of acetoin is highly favored over abstraction at the hydroxyl or methyl hydrogens because of relatively large differences in bond strengths. Formation of complete molecules by radical decomposition as in reaction 2 is somewhat unusual but is consistent with the equality between the quantum yields of methane and carbon monoxide and their chain-like behavior with temperature.

A similar reaction scheme seems a possibility for the photolysis of benzoin and α-substituted benzoins. Kornis and de Mayo report that uv irradiation of benzene solutions of benzoin results in the formation of benzaldehyde in major yield.[32] They further report that irradiation of α-deuteriobenzoin results in a mixture of benzaldehyde and deuteriobenzaldehyde. The situation is confused by the further report that irradiation of α-1-acenaphthenylbenzoin results in 1-acenaphthenyl phenyl ketone; however, benzaldehyde was not formed in appreciable amount. We are continuing our investigation of this and of the mechanisms of process II in general.







The results of the irradiation of 1-hydroxy-2-methyl-3-butanone in the gas phase and in toluene solution with 3130-Å light suggest the reaction scheme of eq III–VI.

$$H_3CCOCH(CH_3)CH_2OH + h\nu \rightarrow$$

$$CH_3\underset{\cdot}{C}O + CH_3\underset{\cdot}{C}HCH_2OH \quad (III)$$

$$CH_3COCH_2CH_3 + CH_2O \quad (IV)$$

$$CH_3CHO + CH_3CH_2CHO \quad (V)$$

$$CH_3CHO + CH_2{=}CHCH_2OH \quad (VI)$$

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The occurrence of reaction III is supported by the detection of methane and carbon monoxide in the gas-phase photolysis and additional products such as biacetyl and *n*-propyl alcohol in the solution phase experiments. The formation of 2-butanone and a polymer in both gas- and solution-phase photolysis suggests the occurrence of reaction IV. Formaldehyde was not isolated but presumably would have polymerized during photolysis. The formation of acetaldehyde and propionaldehyde in equal yield during solution-phase irradiation suggests that reaction V occurs but not VI. The detection of allyl alcohol in solution-phase reactions taken to large conversion could have been due to its formation in a sequence of secondary reactions of the propanol radical formed in reaction III. If reaction V occurs at all, however, one would expect reaction VI to take place also, although at diminished rate due to the decreased lability of primary *vs.* secondary hydrogen atoms. Further work is necessary to settle this question.

Reactions IV–VI presumably arise through cyclic transition state mechanisms. Reaction IV is strictly analogous to the Norrish Type II process, whereas reactions V and VI are Norrish Type III processes. The quantum yields of processes III, IV and V (0.05, 0.03, and 0.01, respectively) indicate that none of these are major pathways of excited-state deactivation in liquid solutions of the β-hydroxy ketone. This is not surprising for process III, since solvent cage effects might be expected to inhibit product formation *via* radical reactions. However, methane, CO, and biacetyl quantum yields were not monitored for the solution phase reactions, and the primary quantum yield of reaction III based on *n*-propyl alcohol production may be underestimated. Neither allyl alcohol nor pinacol was formed in appreciable amounts, and this was taken to mean that all the propyl alcohol radicals which did not react with acetyl radicals were converted to *n*-propyl alcohol by hydrogen atom abstraction from either the solvent or solute.

Reactions V and VI may not be expected to be important in view of recent reports that the Norrish Type III process, *i.e.*, transfer of methyl or methylene hydrogen atoms to the carbonyl oxygen atom *via* a five-membered cyclic transition state, is not an important reaction mechanism in the photolysis of methyl isopropyl ketone[23, 24] and methyl ethyl ketone.[2]

The Norrish Type II process is normally efficient for ketones containing γ-hydrogen atoms and n,π* first excited singlet and lowest lying triplet states ($0.1 < \Phi < 0.5$). Since the n,π* excited carbonyl group is an electrophile[10, 33] the lack of reactivity of the β-hydroxy compound may result from the decreased lability of the hydroxyl hydrogen *atom* as compared with methyl and methylene hydrogen atoms. If this reaction does proceed from an n,π* state, rather than from a high vibrational level of the ground state, then the insensitivity of the quantum yields toward oxygen concentration would indicate that the n,π* *singlet* state is the reactive species.

We are continuing our investigation with this and related compounds in order to compare the effect of molecular structure on the competition between various photoinduced processes. In several cases, excitation of saturated steroidal α-hydroxy ketones has been shown to lead to fission of the bond between the carbonyl and carbinol groups rather than to hydrogen atom transfer.[34] Our results suggest that steric requirements exist which must be met if hydrogen atom transfer is to compete efficiently with other modes of photodecomposition. Further study will define these requirements.

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