Photochemistry in the Adsorbed Layer. VIII. Lifetimes of Excited Alkyl Ketones and Alkyl Radicals Adsorbed on Porous Vycor Glass

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The photolyses as well as the absorption spectra of adsorbed 3-methyl-2-butanone and 3-methyl-2-pentanone have been investigated in the presence and absence of nitrogen monoxide. The Stern-Volmer relationship was applied to the decrease in the rate of photolysis caused by addition of nitrogen monoxide. From the results together with those for acetone, 2-butanone, and 2-pentanone, it has been concluded that in the adsorbed layer the more blue shifted, *i.e.*, the more strongly hydrogen bonded to the surface OH groups a ketone molecule, the shorter the lifetime of its excited state. It has been found that the lifetime of the alkyl radical on the surface increases with the decrease in its ionization potential, leading to the decrease in the strength of its interaction with the surface. Special features of the photolysis in the adsorbed layer have been described for 3-methyl-2-butanone photolysis.

In spite of its importance in many problems,[1] photochemistry in the adsorbed layer appears to be one of the most unexploited fields in photochemistry. We have investigated the photolysis of alkyl ketones such as acetone, 2-butanone, and 2-pentanone adsorbed on porous Vycor glass, as regards general characteristics of the photochemistry in the adsorbed layer, *e. g.*, the enhanced type I selectivity for the ketones having γ-hydrogen atoms, the importance of the reaction of the geminate radical pairs formed in the primary process, and the contribution of surface OH groups to the photochemical reactions.[2-8] Some information on the relative lifetimes of the excited triplet states as well as the radicals on the surface has been obtained from the effect of the addition of nitrogen monoxide upon the photolyses. In the present work, similar studies have been extended to 3-methyl-2-butanone and 3-methyl-2-pentanone in order to obtain more general information on the relative lifetimes of those species as well as the characteristics of the photolysis of adsorbed alkyl ketones.

Experimental

Materials. Commercial compounds (Tokyo Kasei Co., Ltd., Grade SG) were purified by means of preparatory chromatography, and then vacuum distilled bulb-to-bulb. Only those fractions were used which contained less than 0.5% impurity as determined by means of a vapor-phase chromatograph equipped with a flame ionization detector and a polyethylene glycol 1500 column. Porous Vycor glass (Corning, No. 746685-7930) was used as an adsorbent.

Apparatus and Procedure. Details of the apparatus and procedure used in the photolysis in the adsorbed layer were reported.[2-8] A conventional vacuum system was used in conjunction with a special quartz cell capable of studying the spectra and photolysis in the adsorbed layer. The specimen of porous Vycor glass, which had been heated in oxygen to remove carbonaceous impurities, was introduced into the cell and degassed at 500 °C for 7 h. After a certain amount of ketone had been adsorbed on the specimen, photolysis was carried out using an ultra high pressure mercury lamp without filter. Gas phase photolysis was carried out in a cylindrical quartz cell under the same irradiation conditions. The analytical system consisted of three traps and a modified Ward still. The gaseous products were separated by fractional distillation and analyzed by gas-chromatography using a flame ionization detector.

The absorption spectra of adsorbed ketones were determined with a Hitachi EPS 3T type spectrophotometer, measuring transmission through the sample. A quartz cell was placed just before the photomultiplier in order to minimize scattering error. Another porous Vycor glass sample was pretreated under the same conditions in a separate cell and used as a blank in the reference beam. The spectra of the adsorbed ketones increased in intensity proportional to the amounts adsorbed without changes in relative intensity for the bands from 250 to 340 nm.

Results

Photolysis of Adsorbed 3-Methyl-2-Butanone. The major products in the gas phase photolysis of 3-methyl-2-butanone (3-M-2-B) are propylene, propane, and hexane (Table 1). The following processes can be proposed[9,10] for the formation of these products.

$$i\text{-}C_3H_7COCH_3 + h\nu \longrightarrow \begin{cases} i\text{-}\dot{C}_3H_7 + \dot{C}OCH_3 \\ i\text{-}C_3H_7\dot{C}O + \dot{C}H_3 \end{cases} \quad (1)$$

$$i\text{-}\dot{C}_3H_7 + i\text{-}\dot{C}_3H_7 \longrightarrow C_3H_6 + C_3H_8 \text{ or } C_6H_{14} \quad (2)$$

where reaction (1) is α-cleavage of alkyl ketones (type I reaction) and reaction (2) is disproportionation or combination reaction of isopropyl radicals. The rate of propylene formation is larger than the rate of propane formation. Such behavior was found by Zaha and Noyes[9] who attributed it to the occurrence of the following reaction.

TABLE 1. RELATIVE YIELD OF PRODUCTS FROM PHOTOLYSIS OF 3-METHYL-2-BUTANONE AT 25°C

	CH_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	C_6H_{14}
Adsorbed layer[a]	0.005	0.001	10.9	88.7	$<$0.001	$<$0.001
Vapor phase[b]	0.015	6.50	42.1	24.1	5.80	19.4

a) Amount of adsorbed 3-methyl-2-butanone, 8.5×10^{-5} mol/g. Conversion per h, 12—15%. Irradiation time, 15—30 min. b) 3-Methyl-2-butanone pressure, 13.0±0.5 Torr.

$$\dot{R} + i\text{-}C_3H_7COCH_3 \longrightarrow RH + C_3H_6 + CH_3\dot{C}O \quad (3)$$

where R stands for any radicals formed in the primary processes.

In the adsorbed layer photolysis the rate of propane formation is much larger and that of propylene formation much smaller as compared to the corresponding values in the gas phase photolysis. Previous works[4,6] on the photolysis of adsorbed acetone or 2-pentanone show that methane or propane arises from hydrogen abstraction from the surface OH groups by methyl or propyl radicals as well as the disproportionation of the geminate radical pairs such as

$$\dot{C}H_3 + CH_3\dot{C}O \longrightarrow CH_4 + CH_2CO.$$

The reaction of alkyl radicals formed in the primary process with the ketone molecules hardly takes place. A similar situation would be expected for the propane and propylene formation from the photolysis of adsorbed 3-M-2-B. Thus, it can be concluded that in the adsorbed layer the contribution of reaction (3) to the propylene formation is negligible, most part of propylene arising from disproportionation reaction of the geminate radical pairs. It should be noted that the amounts of the radical recombination products such as ethane or hexane are very small in the adsorbed layer. Such behavior is one of the general characteristics of the photolysis of adsorbed alkyl ketones.[4]

In contrast to 3-M-2-B, 3-methyl-2-pentanone (3-M-2-P) undergoes the type II as well as the type I reaction, since it has a γ-hydrogen atom. The most significant feature of its photolysis in the adsorbed layer is a marked enhanced type I selectivity as compared to that in the gas phase photolysis. Details were previously reported[8] (Table 2).

Effect of the Addition of Nitrogen Monoxide upon Photolysis. In order to study the nature of the excited states as well as the radicals formed in the photolysis the effect of the addition of nitrogen monoxide on the photolysis of adsorbed 3-M-2-B and 3-M-2-P has been investigated. In the photolysis of the latter the rate of ethylene formation decreases with increase in the nitrogen monoxide pressure, levelling off to a constant value (Fig. 1). Considering the fact that nitrogen monoxide is an efficient triplet quencher, the amount of quenchable reaction (57%) can be attributed to reaction from the excited triplet state with the remainder of the reaction (43%) occurring from the excited singlet state. A similar nonquenchable fraction of the ethylene formation (44%) has been obtained with the photolysis of adsorbed 2-pentanone in the presence of nitrogen monoxide.[2]

The rate of propane formation from 3-M-2-B as well as that of butane formation from 3-M-2-P decreases markedly with increasing nitrogen monoxide pressure, finally approaching zero around 0.10 Torr for propane and 0.06 Torr for butane, as expected from the action of nitrogen monoxide as a radical scavenger (Fig. 1). In addition to such scavenging action, the decrease in the rate of formation is caused by quenching of the excited states with nitrogen monoxide.

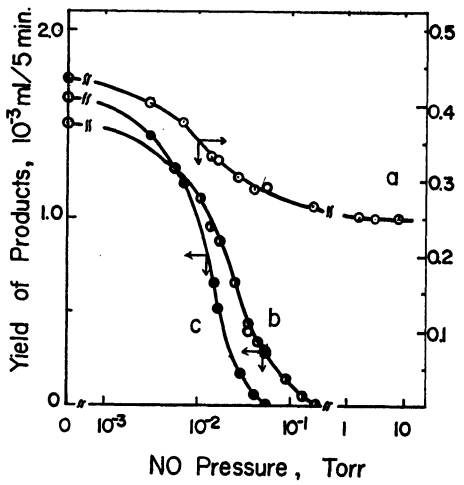

Fig. 1. Effect of nitrogen monoxide upon the rates of photolyses of 3-methyl-2-butanone and 3-methyl-2-pentanone adsorbed on porous Vycor glass.
The amounts of 3-methyl-2-butanone and 3-methyl-2-pentanone adsorbed were 7.5×10^{-5} and 8.5×10^{-5} mol/g, respectively. During the photolysis nitrogen monoxide was somewhat consumed; It was confirmed, however, that the resulting pressure decrease did not affect the value of the constants A and B in the Stern-Volmer equation. a: Ethylene (3-M-2-P), b: propane (3-M-2-B), c: butane (3-M-2-P).

Discussion

The photolysis of adsorbed 3-M-2-B and 3-M-2-P in the presence of nitrogen monoxide is as follows. Reactions (3) and (7) are included only in the case of 3-M-2-P.

$$P + h\nu \longrightarrow {}^1P$$

$${}^1P \xrightarrow{k_1} P + \text{heat} \quad (1)$$

$${}^1P \xrightarrow{k_2} \dot{R} + \dot{C}OR' \quad (2)$$

$${}^1P \xrightarrow{k_3} C_2H_4 + CH_3COCH_3 \quad (3)$$

$${}^1P \xrightarrow{k_4} P + h\nu' \quad (4)$$

$${}^1P \xrightarrow{k_{isc}} {}^3P \text{ (isc)}$$

$${}^3P \xrightarrow{k_5} P + \text{heat} \quad (5)$$

Table 2. Relative yield of products from the photolysis of 3-methyl-2-pentanone at 25°C

	C_2H_4	C_3H_8	C_4H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	type I/II
Absorbed layer[a]	14.1	4.12	3.19	72.6	2.90	3.12	6.0
Vapor phase[b]	73.3	3.15	1.14	12.2	4.18	6.01	0.35

a) Amount of adsorbed 3-methyl-2-pentanone, 4.5×10^{-5} mol/g. Conversion per h, 10—15%. Irradiation time, 15—30min. b) 3-Methyl-2-pentanone pressure, 18.0 ± 0.5 Torr. The selectivity of type type I was identified as follows; $I/II=(\phi_{C_5}+\phi_{C_4}+\phi_{C_3}+\phi_{C_2})/\phi_{C_2H_4}$.

Table 3. Values of A (τk_9) and B ($\tau' k_{11}$) for nitrogen monoxide quenching (M^{-1})

	Acetone[a)]	2-Butanone[a)]	3-Methyl-2-butanone	2-Pentanone[a)]	3-Methyl-2-pentanone
A	—	0.95×10^5	3.6×10^5	2.2×10^5	5.5×10^5
B	0.054×10^6	0.24×10^6	4.9×10^6	6.1×10^6	7.0×10^6

a) Ref. 2.

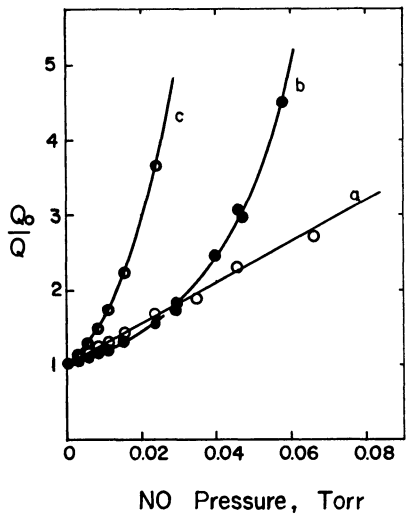

Fig. 2. Stern-Volmer plots for products quenching in the photolyses of 3-methyl-2-butanone and 3-methyl-2-pentanone adsorbed on porous Vycor glass. a; Ethylene (3-M-2-P), b; propane (3-M-2-P), c; butane (3-M-2-P).

$$^3P \xrightarrow{k_6} \dot{R} + \dot{C}OR' \quad (6)$$

$$^3P \xrightarrow{k_7} C_2H_4 + CH_3COCH_3 \quad (7)$$

$$^3P \xrightarrow{k_8} P + h\nu'' \quad (8)$$

$$^3P + NO \xrightarrow{k_9} P + NO \quad (9)$$

$$\dot{R} + [H] \xrightarrow{k_{10}} RH \quad (10)$$

$$\dot{R} + NO \xrightarrow{k_{11}} RNO \longrightarrow \text{Stabilized} \quad (11)$$

$$\dot{R} + R'\dot{C}O \xrightarrow{k_{12}} \text{Recombination or disproportionation products} \quad (12)$$

The α-cleavage from the excited singlet state (reaction 2) can be neglected,[2)] since there exists a striking difference in the reactivity of the excited singlet and triplet states toward α-cleavage of alkyl ketones.[11)] Thus, the following quadratic Stern-Volmer equation is obtained by the steady state treatment for propane formation from 3-M-2-B and butane formation from 3-M-2-P.

$$Q_0/Q = (1+A[NO])(1+B[NO]) \quad (I)$$

where $A=k_9/(k_5+k_6+k_7+k_8)$, $B=k_{11}/([H]k_{10}+[R'CO]k_{12})$. Q and Q_0 are the rates of propane or butane formation in the presence and absence of nitrogen monoxide, respectively. The plot of Q_0/Q against nitrogen monoxide pressure is shown in Fig. 2. Constants A and B for both ketones are so determined to give the best fit to the experimental curves[2)] (Table 3). Values of A and B for other ketones are also given in Table 3.

In the photolysis of 3-M-2-P, ethylene is formed from the singlet as well as the triplet state. The following equation holds for the rate of ethylene formation from the triplet state, which is determined by subtracting the nonquenchable amount of ethylene formed with nitrogen monoxide present from the total amount of ethylene formed without nitrogen monoxide present.

$$Q_0/Q = (1+A'[NO]) \quad (II)$$

where Q and Q_0 are the rates of ethylene formation from the excited triplet state in the presence and absence of nitrogen monoxide, respectively. From the slope of the Stern-Volmer plot (Fig. 2) the value of A' is found to be 5.2×10^5 l/mol, in agreement with that obtained from equation (I). This supports the assumption that the formation of propane and butane from the excited singlet state can be neglected.

Lifetime of Excited Ketone Molecules. The wavelengths of maximum absorption of (n, π^*) transition of adsorbed 3-M-2-B and 3-M-2-P together with the corresponding values of other ketones[3)] are given in Table

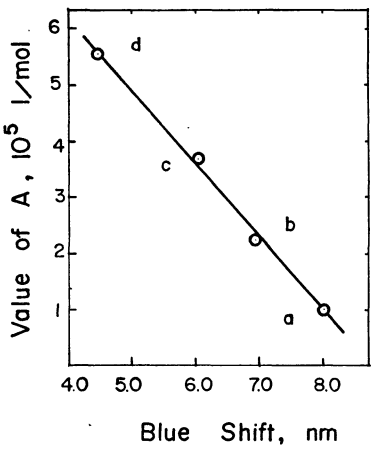

Fig. 3. The relationship between values of A and blue shift. The blue shift was identified as follows; $\Delta E=$ (λ_{max} on Vycor glass) − (λ_{max} in heptane).
a; 2-Butanone, b; 3-M-2-B, c; 2-pentanone, d; 3-M-2-P.

Table 4. Wavelengths of maximum absorption of alkyl ketones adsorbed on porous Vycor glass at 25 °C (nm)

	Acetone	2-Butanone	3-Methyl-2-butanone	2-Pentanone	3-Methyl-2-pentanone
$\lambda_{max.}$ on vycor glass	262.0	270.0	276.0	273.0	280.0
$\lambda_{max.}$ in heptane	276.5	278.0	283.0	279.0	284.5

Table 5. Relative lifetime of the alkyl radicals in the adsorbed layer (M^{-1})

	Methyl	Ethyl	Propyl	Isopropyl	*s*-Butyl
B ($\tau' k_{11}$)	0.054×10^6	0.24×10^6	4.9×10^6	6.1×10^6	7.0×10^6
Relative lifetime	1	11	1100	2800	6400

4. The blue shift of the (n, π^*) bands decreases in the order acetone>2-butanone>3-M-2-B>2-pentanone> 3-M-2-P. Values of A also decrease in the same order (Table 3). A linear relation exists between the values of A and blue shift (Fig. 3). The magnitude of A is mainly determined by the rate of radiationless deactivation k_5, *i.e.*, $k_5 \gg (k_6+k_7+k_8)$.[2] Thus, the results confirms the conclusion that the more blue shifted the ketone molecule, *i.e.*, the more strongly hydrogen bonded to the surface OH groups, the more efficient the radiationless deactivation (k_5).[2]

It is well-known[12] that there is a marked difference between the excited and ground states in the geometry, *e. g.*, the ground state of HCHO is planar, while in its excited singlet state the CO bond makes an angle of 20° to the CH_2 plane. According to the work of Iwata and Morokuma,[13] the hydrogen bond energy of HCHO with water depends upon the geometry in its excited (n, π^*) state, *i.e.*, the extent to which the excited state is non-planar. The Franck-Condon principle shows that the rate of radiationless decay depends upon the vibrational overlap factor.[14] It seems obvious that the overlap factor is expected to be larger the larger the differences in geometry between the ground and excited states. One explanation is as follows. In going from acetone to 3-M-2-P, the extent to which the excited (n, π^*) state is non-planar would decrease in the adsorbed layer, as reflected in the decrease in the strength of the hydrogen bond with the surface OH groups. Such a change in the excited state geometry would affect the rate of the radiationless decay.

Lifetime of Adsorbed Alkyl Radicals. Values of B ($\tau' k_{11}$), including the corresponding values for other ketones obtained previously,[3] are given in Table 5. Although it is expected that in the adsorbed layer the reactivity of the radicals differs from that in the gas phase,[15] it seems difficult to attribute such a large difference in the B values only to the difference in k_{11}.[2,5] It can be concluded that the alkyl radical lifetime increases in the order methyl<ethyl<propyl<isopropyl<*s*-butyl radicals in the adsorbed layer. Assuming that the relative reactivity of nitrogen monoxide toward the radicals in the adsorbed layer is approximately equal to that in the gas phase,[15] it is possible to estimate the relative lifetime of the radicals in the adsorbed layer as seen in Table 5. In the photolysis of adsorbed alkyl ketones the lifetime of alkyl radicals is mainly determined by the rate of recombination of the geminate radical pairs, k_{11}, the magnitude of which is expected to depend upon the surface mobility of the radicals.[6]

According to the work of Garbutt and Gesser,[16] the radicals are stabilized on the surface of porous Vycor glass by charge-transfer interaction where radicals play the role as electron-donors and the surface OH groups as electron-acceptors. In such cases it would be expected that the stabilization energy, *i.e.*, the adsorption energy

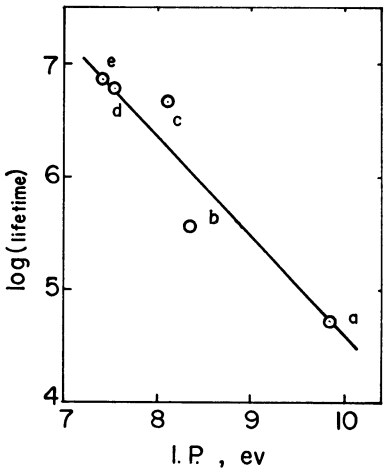

Fig. 4. The relationship between log(lifetime) and ionization potential (I.P.) of alkyl radicals.[17]
a: Methyl, b: ethyl, c: propyl, d: isopropyl, e: s-butyl radical.

of the radicals, E_{ads} decreases with increasing the ionization potential of the donors (radicals). The lifetime of the radical on the surface should increase with the decrease in its surface mobility, which will decrease with increasing adsorption energy of the radical. It is concluded that in the adsorbed layer the lifetime of the radical will increase with the decrease in its ionization potential, *i.e.*, with increasing strength of its interaction with surface. The results shown in Fig. 4 confirm the conclusion.

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