Pergamon

Tetrahedron, Vol. 53, No. 10, pp. 3757-3766, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00096-3

Laser Photolysis of 2-Propanone, 2-Butanone, 3-Pentanone and 3-Buten-2-one in the Gas Phase

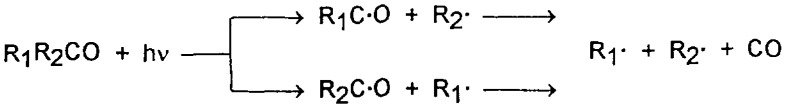
Josef Pola,[a]* Yoshinori Koga[b] and Akihiko Ouchi,[b]*

[a] Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague, Czech Republic

[b] National Institute of Materials and Chemical Research, AIST, MITI, Tsukuba, Ibaraki 305, Japan

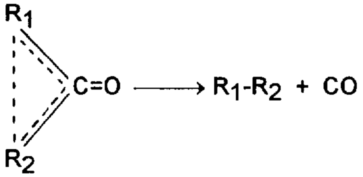
Abstract: Low fluence (25 mJ.cm^{-2}) and high fluence (180 mJ.cm^{-2}) ArF laser (193.3 nm) photolysis of $R_1C(O)R_2$, (R_1, R_2 = CH_3, C_2H_5, C_2H_3) afford carbon monoxide and hydrocarbons which are in the former case mostly R_1-R_2 alkanes and in the latter case R_1-R_2 alkanes along with methane, ethene and ethyne. The effect of excess of helium and hydrogen suggests that the products preferred at the high-fluence result from reactions of hot $CH_3\cdot$ radicals, and disproportionations of $C_2H_5\cdot$ and cross disproportionation of $CH_3\cdot$ radicals. No effect of radical scavenging [$^2H_4$]germane on the course of the low-fluence photolysis is judged to reflect high energy content of R_1 and R_2 radicals.
© 1997 Elsevier Science Ltd. All rights reserved.

The gas-phase lamp-induced photolysis of aliphatic ketones $R_1C(O)R_2$ without γ-hydrogen next to a C=O bond has been extensively studied at low intensities and low photon energies matching the n→π* absorption band centered at ~ 280 nm.[1] It is commonly regarded that (1) the initial step under these conditions is the Norrish "Type I" split into $R_1\cdot + R_2C\cdot O$ (and $R_2\cdot + R_1C\cdot O$) radicals, which loses selectivity with increasing energy of the photon, and that (2) hot RC·O radicals undergo decomposition into R· and CO (Scheme 1).



Scheme 1

At higher incident photon energies from ArF laser (193.3 nm) the excitation into the 3s-n Rydberg transition affords directly CO and $R_1\cdot$ and $R_2\cdot$ radicals.[2] The radicals occurrence had been earlier established through scavenging experiments (Hg, I_2, HI) and the determination of final products[1] formed by radical combination and recently confirmed by time resolved techniques in the photolysis of 2-propanone[2a-e] and 3-buten-2-one[2f]. The final R_1-R_2 products can, in principle, be also formed by a molecular expulsion (Scheme 2) which has been until recently assumed to occur as only a negligible pathway[1a,b,3] and the detection of which by using various radical traps is not straightforward[1a].



Scheme 2

We have recently reported[4] that [$^2H_4$]germane is an efficient trap for $CH_3\cdot$ radicals produced in the mercury-lamp-induced but not in the ArF laser-induced photolysis of 2-propanone; we explained[4] the same course of the ArF laser-induced photolysis of 2-propanone at the laser intensity ~ 2 MW.cm^{-2} in the absence and presence of [$^2H_4$]germane by a split of the two methyl groups and the recombination of the two simultaneously generated $CH_3\cdot$ radicals within the molecular sphere. Similar molecular channel leading to CO and ethyne/ethene has been established for the ArF laser photolysis of propenal and propynal[5a], and for the XeCl laser photolysis of adamantan-2-one[5b] .

In this paper we report on the distribution of photolysis products in the ArF laser photolysis of $CH_3C(O)CH_3$, $CH_3C(O)C_2H_5$, $C_2H_5C(O)C_2H_5$ and $CH_3C(O)CH{=}CH_2$ at different laser fluence and in the presence of hydrogen, helium and [$^2H_4$]germane, and explain it in terms of mostly radical reactions. The observed absence of the effect of [$^2H_4$]germane on the ArF laser photolysis of all the ketones is regarded to be caused by concentration effects and/or internal excitation of radicals.

Results and Discussion

The gaseous ketones $R_1C(O)R_2$ possess a strong absorption band in the region of the 193.3 nm emission of the ArF laser, which is much more intense than their absorption band peaked at ~ 280 - 310 nm (Fig. 1; R_1, R_2 - λ_{max} in nm (absorptivity in 10^{-3} kPa^{-1}.cm^{-1}):

CH_3, CH_3 - 194 (26); CH_3, C_2H_5 - 195 (30); C_2H_5, C_2H_5 - 196 (34) and $H_2C{=}CH$, CH_3 - 212 (51).

The ArF laser irradiation of these ketones results in the formation of carbon monoxide (observed by IR spectroscopy at 2140 cm^{-1}) and hydrocarbons (determined by gas-chromatography). The

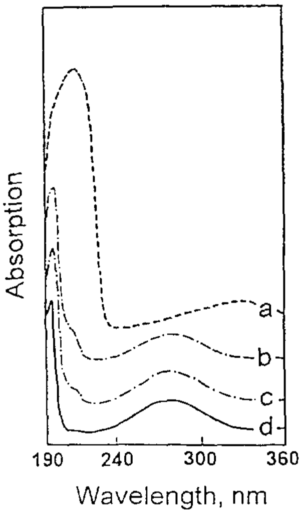


Fig. 1
UV spectra of 3-buten-2-one (a), 3-pentanone (b), 2-butanone (c), and 2-propanone (d).

search for carbonyl group-containing products and higher molecular weight products by FTIR spectroscopy and GC revealed that none of such compounds were produced in detectable quantities. The photolysis of 3-buten-2-one was accompanied with the formation of a solid material deposited as films on all the inside of the reactors. This material is opaque to the ArF laser radiation and detrimental to photolysis progress. Important features of all the photolyses is an almost invariant distribution of hydrocarbon products throughout all the photolysis range studied. Quantities of hydrocarbons given throughout the paper are in molar per cent.

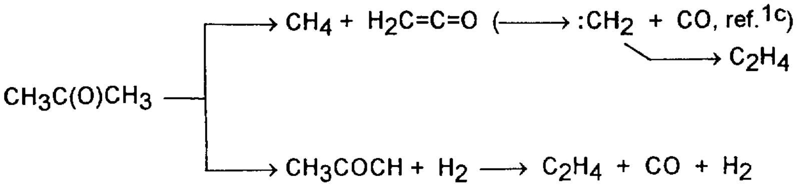
2-Propanone

Photolysis of 2-propanone (5.3 kPa) at the low irradiation fluence (25 mJ.cm^{-2}) is dominated by the formation of ethane (85 - 94 %); methane (5 - 10 %), propane (0.4 - 3 %) and ethene (0.7 - 2 %) were the minor products (Fig. 2a).

At the high fluence (180 mJ.cm^{-2}), amounts of ethane decrease (44 - 49 %), while methane (21 - 23 %) and ethene (14 - 15 %) are produced in higher amounts together with ethyne (15 - 19 %) and propane (1 - 2 %) (Fig. 2b). The amounts of these hydrocarbons produced at the higher fluence are significantly affected by the excess of hydrogen or helium. Thus the irradiation of $(CH_3)_2CO$ (5.3 kPa) - He (75 kPa) gives more ethane (~ 65 %) and less methane (~ 18 %), ethene (~ 9.5 %) and ethyne (~ 7 %), while that of $(CH_3)_2CO$ (5.3 kPa) - H_2 (75 kPa) affords more ethane (62 %) and methane (28 %), and less ethene (~ 5.5 %) and ethyne (~ 2.7 %).

The formation of the hydrocarbons in the low fluence photolysis can be interpreted by the homolytic C-C fissions, the $CH_3\cdot$ radicals combination and the H-abstraction by $CH_3\cdot$ radicals[1], and also by molecular extrusion of ethane[4]. The laser photolysis at 25 mJ.cm^{-2} of $(CH_3)_2CO$ (3 kPa) - GeD_4 (7 kPa) driven to 10 % conversion results in the depletion of 1 % of GeD_4 and affords ethane (83 %), methane (14 %) and ethene (3 %), the amounts being very similar to those obtained in the absence of this radical scavenger[4,6]. Similar absence of the radical scavenging effect of GeD_4 at 70 mJ.cm^{-2} was earlier ascribed by us[4] to the operation of molecular expulsion of C_2H_6. This mechanism was, however, not noted under similar conditions[2a-e,2g]. Alternative explanation of the inefficiency of GeD_4 to scavenge $CH_3\cdot$ radicals can involve the fact that ability of GeD_4 to react in [D] abstraction depends on energy content of $CH_3\cdot$ radicals. Different reactivity of radicals in H-abstraction reactions is known (see e.g. ref.[7]).

The significant formation of ethene and ethyne in the high fluence photolysis of 2-propanone has not been previously observed. The effects of hydrogen and helium in these experiments suggest the occurrence of hot $CH_3\cdot$ radicals which are deactivated by He and H_2 to yield ethane and reacted with H_2 to give methane. Ethene can be produced by molecular channels earlier proposed in



Scheme 3

the low fluence photolysis to explain minor products (Scheme 3, refs.[2b,8]), or by the decomposition $CH_3\cdot \rightarrow :CH_2 + H$ (ref.[2b]) and $:CH_2$ recombination (ref.[8]). Direct irradiation of ethene (1.7 kPa) at 193 nm (fluence 180 mJ.cm^{-2}) affords C_2H_2 in yields about 10 times lower than achieved in the photolysis of 2-propanone. This indicates that ethyne can be only produced by photolysis of a hot C_2H_4. Such a $C_2H_4^*$ photolysis can afford excited $C_2H_3\cdot$ radical which either dissociates[9] into C_2H_2 + H or disproportionates into C_2H_2 and C_2H_4. Methane is apparently formed by the disproportionation between $CH_3\cdot$ and $H_2C{=}CH\cdot$ radicals ($\rightarrow CH_4 + C_2H_2$) and by combination $CH_3\cdot + H\cdot \rightarrow CH_4$, but a molecular elimination channel $CH_3C(O)CH_3 \rightarrow CH_4 + CH_2CO$ observed in the 147 nm photolysis[9] and/or H-abstraction by hot $CH_3\cdot$ radical from the parent molecule[10] or from ethane cannot be excluded.

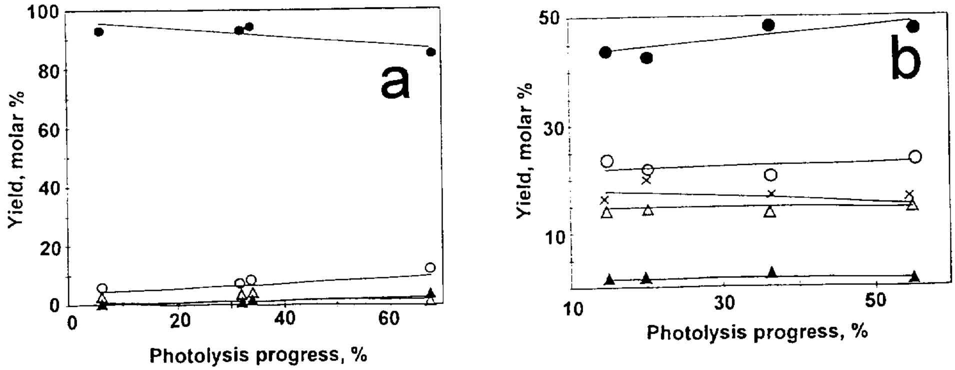


Fig. 2
Distribution of products in photolysis of 2-propanone at the low (a) and high (b) irradiation fluence.
● C_2H_6, ○ CH_4, △ C_2H_4, ▲ C_3H_8, x C_2H_2.

3-Pentanone

Photolysis of 3-pentanone (4 kPa) at the low irradiation fluence (25 $mJ.cm^{-2}$) yields n-butane as a major product (62 - 70 %) together with smaller amounts of propane (11 - 13 %), ethene (13 - 14 %), ethane (8 - 10 %), ethyne (~ 1 %) and methane (~ 0.5 %) (Fig. 3 a).

At the high fluence (180 $mJ.cm^{-2}$), the production of n-butane diminishes (17 - 20 %) and it is comparable to that of ethane (20 - 25 %), ethene (18 - 23 %) and propane (19 - 22 %), but it is still higher than that of ethyne (10 - 13 %) and methane (9 - 10 %) (Fig. 3 b). The yields of n-butane (~ 22 %) are very little increased and those of ethyne (9 %) and methane (~ 5 %) are somewhat lower when the high fluence irradiation is carried out with $(C_2H_5)_2CO$ (4 kPa) - He (75 kPa) mixtures. The formation of n-butane (35 - 40 %) is more increased in the excess of hydrogen (the irradiation of $(C_2H_5)_2CO$ (4 kPa) - H_2 (75 kPa) mixtures) while that of methane (~ 3 %) and ethyne (~ 6 %) is decreased.

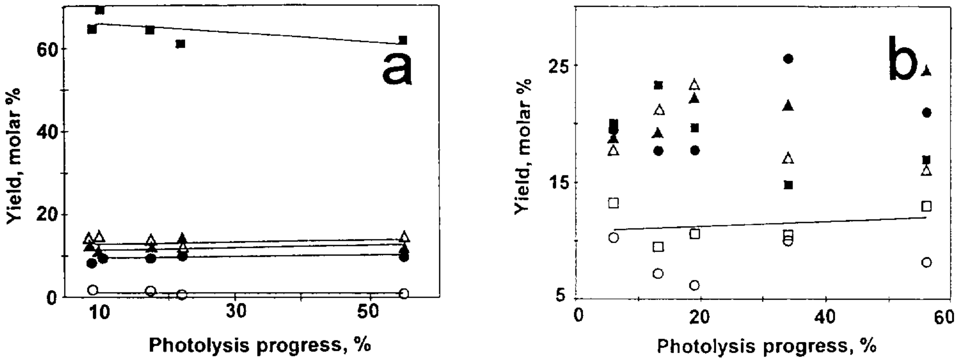


Fig. 3

Distribution of products in photolysis of 3-pentanone at the low (a) and high (b) irradiation fluence. ■ C_4H_{10}, △ C_2H_4, ▲ C_3H_8, ● C_2H_6, ○ C_2H_2, □ CH_4,

The production of n-butane, ethane and ethene at the low fluence can be accounted for, similarly as for the photolysis of 3-pentanone at 313 nm with low intensitiy light[1a], by Norrish I type cleavage and by combination and disproportionation of $C_2H_5\cdot$ radicals. The substantial amounts of the other products, namely those of propane and methane can be reconciled by assuming the decomposition of hot ethane[11] into methyl radicals ($C_2H_6 \rightarrow 2\ CH_3\cdot$) and the cross disproportionation ($CH_3\cdot + C_2H_5\cdot \rightarrow CH_4 + C_2H_4$) and combination ($CH_3\cdot + C_2H_5\cdot \rightarrow C_3H_8$) reactions. The almost invariant ratios of the products (Fig. 3 a) allow to extract the disproportionation-combination ratio k_d/k_c for ethyl radical 0.13 ± 0.1, and the cross disproportionation-combination ratio k_d/k_c for methyl and ethyl radical 0.042 ± 0.002 both of which are in a very good accord with the earlier reported values.[12]

The laser photolysis at 25 $mJ.cm^{-2}$ of $(C_2H_5)_2CO$ (2.7 kPa) - GeD_4 (7.3 kPa) driven to 12 % conversion results in 3 % depletion of GeD_4 and affords hydrocarbons in the following relative amounts: ethane (0.10), ethene (0.26), propane (not determined due to identical retention times of GeD_4 and propane), and butane (1.0). No increase in quantities of ethane (C_2H_5D) indicates that trapping of C_2H_5 radicals by GeD_4 does not take place. This finding might be in line with the occurrence of molecular expulsion of n-butane. However, the small amounts of propane, ethene and ethane formed in these low fluence experiments prove the formation of $CH_3\cdot$ and $C_2H_5\cdot$ radicals and indicate that C_2H_5 and CH_3 radicals do not react with GeD_4.

The amounts of hydrocarbons produced at the high fluence suggest the formation of hot ethane, its decomposition into 2 CH_3 radicals, and the occurrence of the aforementioned reactions of CH_3 radicals. Thus, the significant formation of ethyne is compatible with a reaction sequence $CH_3\cdot \rightarrow :CH_2 + H$, $2\ :CH_2 \rightarrow C_2H_4 \rightarrow C_2H_3\cdot + H$, and $2\ C_2H_3\cdot \rightarrow C_2H_4 + C_2H_2$ as proposed in the case of the high fluence photolysis of 2-propanone. The effect of the excess of hydrogen and helium, which should mostly consist in collisional deactivation of hot radicals (and hot C_2H_6 molecule), is supportive of this view.

2-Butanone

Photolysis of 2-butanone (8 kPa) at the low fluence (25 mJ.cm^{-2}) affords propane (40 - 42 %), ethane (29 - 32 %), n-butane (14 - 16.5 %), ethene (8.5 - 10 %), methane (3 - 4 %), ethyne and propene (both < 1 %) (Fig. 4 a).

At the high fluence (180 mJ.cm^{-2}), the formation of propane (19 - 29 %) and butane (6 - 8 %) is decreased, ethane (19 - 26 %) is produced in similar amounts as with the low fluence, and the yields of ethene (20 - 25 %), methane (10 - 15 %) and ethyne (5 - 7 %) are increased. Small quantities of propene (~ 2 %) and butene (~ 0.5 %) are formed, too (Fig. 4 b). The high fluence irradiation into $CH_3C(O)C_2H_5$ (8 kPa) - He (or H_2) (75 kPa) afforded these products in practically the same amounts : propane (22 - 24 %), butane (6 - 8.5 %), ethane (25 - 27 %), methane (10 - 12 %), ethene (19 - 22 %) and ethyne (7 - 8 %).

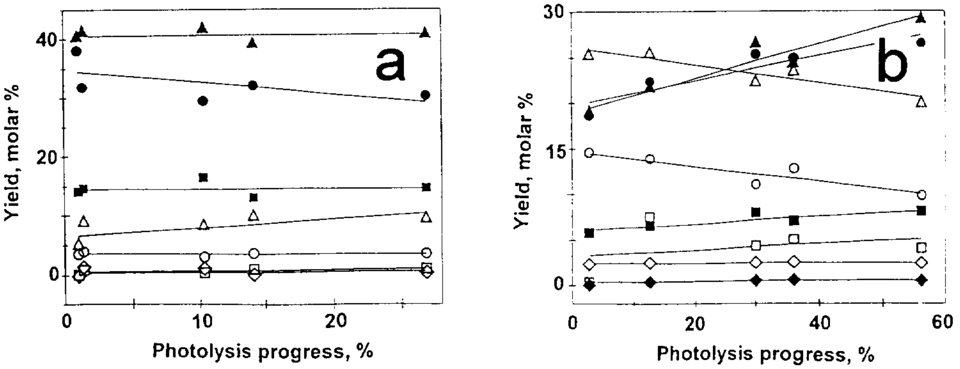
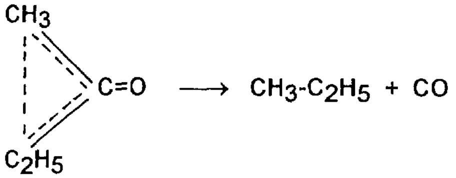


Fig. 4
Distribution of products in photolysis of 2-butanone at the low (a) and high (b) irradiation fluence.
▲ C_3H_8, ● C_2H_6, ■ C_4H_{10}, △ C_2H_4, ○ CH_4, □ C_2H_2, ◇ C_3H_6, ♦ C_4H_8.

The formation of propane, ethane, butane and ethene might have been explained solely by the α-C-C bond cleavages of 2-butanone and by the disproportionation of $C_2H_5\cdot$ radical and recombinations of $CH_3\cdot$ and $C_2H_5\cdot$ radicals. We note that the disproportionation of the ethyl radical was not observed in previous examinations using lamps as irradiation source[1a-c,13], in which only products of alkyl radical recombinations (ethane, propane and butane) were produced in approximately equal amounts. The almost constant ratios of the products at the low fluence observed in our experiments (Fig. 4 a) might have been fitted by radical combinations (2 $CH_3\cdot \rightarrow C_2H_6$, $CH_3\cdot + C_2H_5\cdot \rightarrow C_3H_8$, and 2 $C_2H_5\cdot \rightarrow C_4H_{10}$), $C_2H_5\cdot$ disproportionation and cross disproportionation ($CH_3\cdot + C_2H_5\cdot \rightarrow CH_4 + C_2H_4$). This would have yield k_d/k_c (C_2H_5) 0.39 ±0.02 and k_d/k_c (CH_3) 0.085 ±0.005, the values distinctively higher than those reported for the gas phase previously.[12] However, the unequal yields of the products of the radical combinations (i.e. the observed preference for propane (1.0) over ethane (0.60) and butane (0.40) support some contribution of molecular extrusion (eq.1).



$$\begin{matrix} CH_3 \\ \quad C{=}O \\ C_2H_5 \end{matrix} \longrightarrow CH_3\text{-}C_2H_5 + CO \qquad (1)$$

The unusually high values of k_d/k_c indicate that ethene can be also formed by an additional channel (2).

$$CH_3\cdot + C_2H_5COCH_3 \longrightarrow CH_4 + H_2C{=}CH_2 + CO + CH_3\cdot \qquad (2)$$

The amounts of hydrocarbons at the high fluence can be explained, similarly as in the case of laser photolysis of 2-pentanone, by the formation of hot ethane molecule, and its cleavage into methyl radicals, and by $CH_3\cdot \rightarrow :CH_2 + H$, 2 $:CH_2 \rightarrow C_2H_4$, and $C_2H_4 \rightarrow C_2H_3\cdot + H$, and 2 $C_2H_3\cdot \rightarrow C_2H_4 + C_2H_2$ reactions.

3-Buten-2-one

Photolysis of 3-buten-2-one (8 kPa) at the fluence 25 mJ.cm^{-2} yields, in the order of decreasing importance, propene (26 - 31 %), ethane (20 - 22 %), ethyne (19 - 23 %), ethene (11 - 13 %), methane (7 - 9 %), buta-1,3-diene (4 - 4.5 %) and propyne (~ 0.5 %) (Fig. 5). This products distribution is not affected by the excess of helium. The important feature of the photolysis is deposition of a yellowish film on the inside of the reactor, which is opaque to 193 nm radiation and detrimental to the photolysis progress. The solid material is produced by ~ 5 - 10 % of 3-buten-2-one.

The observed gaseous products can be explained by the α-C-C splits of the ketone and successive combination (2 $C_2H_3\cdot \rightarrow C_4H_6$, $C_2H_3\cdot + CH_3\cdot \rightarrow C_3H_6$, and 2 $CH_3\cdot \rightarrow C_2H_6$) and disproportionation (2 $C_2H_3\cdot \rightarrow C_2H_2 + C_2H_4$, $CH_3\cdot + C_2H_3\cdot \rightarrow CH_4 + C_2H_2$) reactions. These reactions together with the decomposition of hot vinyl radicals ($C_2H_3\cdot^* \rightarrow C_2H_2 + H$) and the reaction of vinyl and methyl radicals with hydrogen ($C_2H_3\cdot + H \rightarrow C_2H_4$, $CH_3\cdot + H \rightarrow CH_4$) were also assumed to explain the yields of final products of ArF laser photolysis at fluences 5 - 10 mJ.cm^{-2} wherein no solid products have been reported.[2f] The other different feature observed

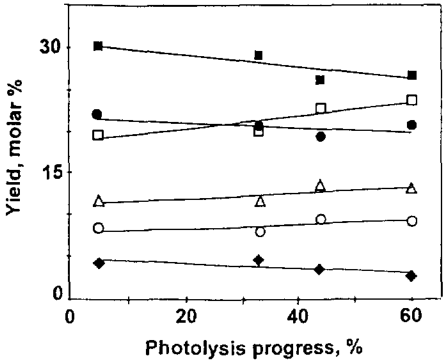


Fig. 5
Distribution of products in photolysis of 3-buten-2-one at the low irradiation fluence.
■ C_3H_6, □ C_2H_2,● C_2H_6, Δ C_2H_4, O CH_4, ♦ C_4H_6.

under our conditions is the prevalence of propene over butadiene, which gives $k_d/k_c(CH_2{=}CH\cdot) \sim 2.9$, the value much higher than ~ 0.31 determined for the lower fluences in ref.[2f]. We note that the high value is comparable with those for t-butyl and alkoxy radicals.[12] We observed no effect of the excess of He on the distribution of final products and this suggests that (i) $C_2H_3^* \rightarrow C_2H_2 + H$ is only a minor reaction, (ii) the vinyl radical disproportionation is a major source of ethene and ethyne, and (iii) the excess of C_2H_2 over C_2H_4 is caused by the cross disproportionation $CH_3\cdot + C_2H_3\cdot \rightarrow CH_4 + C_2H_2$. The unequal yields of the products of the radical combinations (i.e. the observed preference for propene (1.0) over ethane (0.73) and buta-1,3-diene (0.15) is in line with a contribution of molecular extrusion of $CH_3\cdot$ and $H_2C{=}CH\cdot$ moieties. We assume that a fraction of $H_2C{=}CH\cdot$ radicals takes part in a polymerization (the production of the solid material) and that that reaction is responsible for a decrease in amounts of buta-1,3-diene and propene.

General remarks

We show that the products of the 193 nm photolysis of $R_1C(O)R_2$ ketones significantly differ depending whether the low (25 mJ.cm^{-2}) or high (180 mJ.cm^{-2}) irradiation fluences are used. The photolyses afford carbon monoxide and hydrocarbons which are in the former case mostly R_1-R_2 alkanes and in the latter case R_1-R_2 along with methane, ethene and ethyne. These products can be rationalized in terms of concurrently proceeding reactions of $R_1\cdot$ and $R_2\cdot$ radicals (reactions of hot $CH_3\cdot$ radicals and disproportionation reactions of $C_2H_5\cdot$ and $CH_3\cdot$ radicals), and some contribution of molecular elimination of R_1-R_2. The molecular channel gets support from the higher amounts of R_1-R_2 over R_1-R_1 and R_2-R_2 products in the low fluence experiments. The observed nonexistence of the effect of [$^2H_4$]germane, an efficient trap of $CH_3\cdot$ radicals in the lamp-induced photolysis of 2-propanone[4], does not appear to be unambiguous evidence for the absence of radicals. No occurrence of [D] abstraction by $R_1\cdot$, $R_2\cdot$ and $CH_3\cdot$ radicals which are undoubtfully formed in the course of the laser photolysis of all the ketones may be related to a decrease of reactivity of these radicals towards GeD_4 when they are produced at 193.3 nm. The absorption of the radiation at 193.3 nm and that tuned to the n→π* absorption band centered at ~ 280 nm correspond to ca. 620 kJ.mole^{-1} and 390-430 kJ.mole^{-1}, respectively. This indicates that radicals produced in the former case are more internally excited (see refs.[2g,15]) and we surmise that the lack of reactivity of the radicals toward GeD_4 is associated with radicals excited state, or with high concentration of radicals in the region of laser beam which favours self-reactions of radicals.

Experimental

Laser photolysis experiments were performed on gaseous samples of $CH_3C(O)CH_3$ (5.3 kPa), $CH_3C(O)C_2H_5$ (8.0 kPa), $C_2H_5C(O)C_2H_5$ (4.0 kPa) and $CH_3C(O)CH=CH_2$ (8.0 kPa) by using an EMG 201 MSC Lambda Physik (ArF) laser operating at 193.3 nm with repetition frequency 10 Hz.

The samples were irradiated in two different reactors. The one reactor consisted of two orthogonally positioned tubes (both 3 cm in diameter), one (13 cm long) fitted with KBr windows and the other (9 cm long) furnished with quartz windows. The other reactor was all quartz tube (10 cm long, 3 cm in diameter). Both reactors were equipped with a side-arm fitted with a rubber septum and a side-arm with a valve connecting them to a standard vacuum manifold. The laser beam of different fluences (full width at half maximum typically 23 ns) was passed through a slit and its output energy was monitored by a Gentec ED-500 joulemeter connected to a Tektronix T912 10 MHz storage oscilloscope.

The progress of the photolyses was monitored by gas chromatography. The GC analyses to determine quantities of hydrocarbons and ketones after the irradiation were performed on Gasukuro Kogyo model 370 chromatographs (one with a 60 m x 0.25 mm I.D. Neutra Bond-1 capillary column (GL Sciences, Inc.) and another with a packed 2m x 3 mm I.D. Unipak S SUS column (GL Sciences Inc.)); sampling was conducted after expansion of helium into the reactor by a gas-tight syringe (Dynatech Precision Sampling). Both chromatographs were equipped with flame-ionization detectors and coupled with a Shimadzu CR-4A Chromatopac data processor. The photolytic progress with $CH_3C(O)CH=CH_2$ was also monitored by FTIR spectroscopy (a Shimadzu FTIR-4000 spectrometer) using diagnostic absorption bands of the ketones at 1075 cm^{-1}.

The photolytic products were identified by the gas chromatography using the comparison of retention times with those of standard hydrocarbons, and also by a Shimadzu GC-MS-QP 1000 EX spectrometer.

The UV absorption spectra of all the ketones in the gas phase expanded in the reactors were recorded by using a Shimadzu UV-2100 spectrometer.

Photolyses of ketones - H_2, ketones - He, and ketones-GeD_4 mixtures were carried out in both reactors. The progress of the decomposition of GeD_4 was followed by using absorption band at 1520 cm^{-1} (absorption coefficient 0.059 kPa^{-1}.cm^{-1}).

2-Propanone, 2-butanone (both Wako Pure Chemical Industries, Ltd.), 3-buten-2-one and 3-pentanone (both Tokyo Kasei Kogyo Co., Ltd.) were commercial samples which were degassed prior to use. [$^2H_4$]germane was prepared as reported previously[14].

Acknowledgements

J.P. gratefully acknowledges his visiting Fellowship at National Institute of Materials and Chemical Research funded by MITI.

REFERENCES

1. (a) Calvert, J. G.; Pitts, J. N. *Photochemistry*, Wiley, New York, **1966**.
   (b) Bérces,T. in *Comprehensive Chemical Kinetics*; Bamford, C. H.; Tipper, C. F. H. Eds., Elsevier, Amsterdam, **1972**.
   (c) Lee, E. K. C.; Lewis, R. S. *Adv. Photochem.* **1980**, 12, 1.
   (d) Yamashita, S. *J. Chem. Soc. Jpn.* **1976**, 49, 188.
2. (a) Adachi, H.; Basco, N.; James, D. G. L. *Chem. Phys. Lett.* **1978**, 59, 502.
   (b) Lightfoot, P. D.; Kirwan, S. P.; Pilling, M. J. *J. Phys. Chem.* **1988**, 92, 4938.
   (c) Woodbridge, E. L.; Fletcher, T. R.; Laufer, A. H., *J. Phys. Chem.* **1993**, 97, 1502.
   (d) Strauss, C. E. M.; Houston, P. L. *J. Phys. Chem.* **1990**, 94, 8751.
   (e) Hall, G. E.; Van den Bout, D.; Sears, T. *J. Chem. Phys.* **1991**, 94, 4182.
   (f) Fahr, A.; Braun, W.; Laufer, A. H. *J. Phys. Chem.* **1993**, 97, 1502.
   (g) North, S. W.; Blank, D. A.; Gezelter, J. D.; Longfellow, C. A.; Lee, Y. Y. *J. Chem. Phys.* **1995**, 102, 4447.
3. Potzinger, P.; Von Bunau, G. *Ber. Bunsenges. Phys. Chem.* **1968**, 72, 195.
4. Pola, J.; Taylor, R. *Tetrahedron Lett.* **1994**, 35, 2799.
5. (a) Haas, B.-M.; Minton, T.; Felder, P.; Huber, R. *J. Phys. Chem.* **1991**, 95, 5149.
   (b) Ichinose, N.; Kawanishi, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2017.
6. (a) Ballestri, M.; Chatgilialoglu, C.; Guerra, M.; Guerrini, A.; Lucarini; M.; Seconi, M. *J. Chem. Soc., Perkin Trans. 2*, **1993**, 421.
   (b) Clark, K. B.; Griller, D. *Organometallics* **1991**, 10, 746;
   (c) Lucztyk, J.; Maillard, B.; Deycard, S.; Lindsay, D. A.; Ingold, K. U. *J. Org. Chem.* **1987**, 52, 3509.
7. Pola, J.; Taylor, R. *J. Organometal. Chem.* **1993**, 446,131.
8. Lin, L. J.-T.; Ausloos, P. *J. Photochem.* **1972**, 1, 453.
9. Stolow, A.; Balko, B. A.; Cromwell, E.; Zhang, J.; Lee, Y. T. *J. Photochem. Photobiol., A : Chem.* **1992**, 62, 285.
10. MacPherson, M. T.; Pilling, M. J.; Smith, M. J. C. *J. Phys. Chem.* **1985**, 89, 2268.
11. Thrush, B. A. *Proc. Roy. Soc. (London)*, A **1958**, 243, 555.
12. Gibian, M. J.; Corley, R. C. *Chem. Rev.* **1973**, 73, 441.
13. (a) Durham, R. W.; Martin, G. R.; Sutton, H. C. *Nature*, **1949**, 164, 1052.
    (b) Martin, G. R.; Sutton, H. C. *Trans. Faraday Soc.* **1952**, 48, 823.
14. Pola, J.; Parsons, J. P.; Taylor, R. *J. Chem. Soc., Faraday Trans.* **1992**, 88, 1637.
15. Hall, G. E.; Vanden Bout, D; Sears, T. J. *J. Chem. Phys.* **1991**, 94, 4182.

(*Received in UK* 28 *November* 1996; *accepted* 23 *January* 1997)