CO_2 LASER-INDUCED DECOMPOSITION OF ACETONE, 2,3-BUTANEDIONE AND CYCLOBUTANONE SENSITIZED BY SULFUR HEXAFLUORIDE

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The CO_2 *cw* laser powered homogeneous pyrolysis (LPHP) of acetone, 2,3-butanedione and cyclobutanone (all 1·3—4 kPa) sensitized by sulphur hexafluoride (0·7—1·3 kPa) was investigated. The decomposition course of the ketones is analogous to that occurring under conventional pyrolytic conditions. The decomposition rate and the product composition are affected by laser power, partial pressure of the sensitizer, and the buffer gas (helium) added. Besides the conventional pyrolytic products, the LPHP of acetone and 2,3-butanedione affords acetylene and that of cyclobutanone produces acetic acid. A possible reaction mechanism of the decompositions is discussed.

Considerable interest in the use of infrared lasers to stimulate or augment chemical reactions exists in the recent literature[1–5]. While specific reaction pathways of molecules absorbing infrared photons appear, contrary to early expectation, sparse and dificultly to find, the thermal decomposition of organic compounds accomplished by infrared lasers holds a promise for the thermal chemistry. A great effort in this field to find new set-ups or procedures for conducting mono- or bimolecular reactions in the gas phase is still recognizable[6–8]. The LPHP technique[9] enables fast intermolecular vibrational-translational energy transfer between infrared radiation absorbing molecules of the same compound, or between absorbing molecules of one and non-absorbing molecules of other compound(s). The reactant temperature can be fastly increased in a homogeneous way up to temperatures as high as 1 500°K, this being unrealizable in classical or pulsed pyrolysis. The experimental arrangement eliminates the effect of walls and may thus affect the course of thermally initiated reactions proceeding by a radical mechanism.

Thermal decomposition of acetone[10–12] and 2,3-butanedione[13–16] proceeds by a radical mechanism and that of cyclobutanone is a molecular process[17–19]. As a part of our program to investigate the possibility of inducing organic reactions by infrared lasers we report in this paper on the LPHP of acetone, 2,3-butanedione and cyclobutanone induced by a *cw* CO_2 laser and sensitized by sulphur hexafluoride with the aim to gain knowledge whether the LPHP of these compounds differs from the decomposition conducted.under conventional pyrolytic conditions.

EXPERIMENTAL

Reagents. Acetone (*p.a.*, Lachema Brno), cyclobutanone (Fluka AG, Buchs), 2,3-butanedione (Koch-Light Laboratories, Coinbrook Bucks), sulphur hexafluoride (I.E.C. standard, Montedison, Milano) and helium (TEGA, Leipzig) were pure commercial products.

Instrumentation and analytical technique. The experiments were performed in the commercial infrared spectroscopical gas cell (C. Zeiss, Jena, 10-cm path length, 4·5-cm inner diameter). Before entering the gas cell samples of sulphur hexafluoride and the degassed ketone were premixed on a standard vacuum line. The mixtures were irradiated by a CO_2—N_2—He *cw* laser[20] operated at 931 cm^{-1} (the P(34) line, $00^{0}1 \rightarrow 10^{0}0$ transition). The laser beam was focused with Ge lens (25 cm f.l.). The decomposition products were identified by comparison of infrared spectra with those of authentic samples. The reactants disappearance and products appearance were monitored with a Perkin-Elmer Model 621 infrared spectrophotometer. Partial pressure of products was calculated from optical densities at suitable wavelengths.

RESULTS AND DISCUSSION

Acetone

The product composition during the irradiation of the acetone (1·9 kPa) – SF_6 (1·3 kPa) mixture by the *cw* CO_2 laser is given in Fig. 1. The conversion of the acetone decomposition is markedly dependent on the laser power used – when the acetone–SF_6 mixture was irradiated by using the laser power of 18 W the decomposition effectively occurs, but it did not proceed with the laser power of 8 W or lower. The products formed by the sensitized acetone decomposition are (numbers in parentheses show partial pressure of the products in kPa at the end of the experiment (80 s)): methane (1·5), carbon monoxide (1·9), ethylene (0·1), acetylene (0·2) and ketone (0).

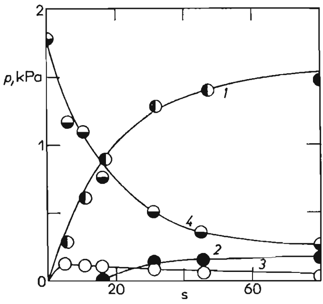


FIG. 1

The Dependence of the Product Composition on the Irradiation Time (*1* methane, *2* acetylene, *3* ketene) for the Decomposition of Acetone (*4* 1·9 kPa) Induced by the CO_2 Laser Irradiation in the Presence of SF_6 (1·3 kPa)

Methane and ketene are typical products of thermal decompositions of acetone[10-12] proceeding by a radical mechanism and studied in the range <0·1 – 100 kPa and 500–750°C (Eq. (*A*)).

$$CH_3COCH_3 \rightarrow CH_4 + CH_2{=}C{=}O \qquad (A)$$

The LPHP of acetone in the presence of SF_6 is apparently of the same mechanism and differs from the classical thermal decomposition by somewhat dissimilar product composition, mainly by a small amount of arising ketene (Fig. 1). The amount of methane formed and the methane formation rate during the irradiation correspond roughly to the decrease in amount of acetone and to the rate of acetone disappearance. Ketene is known[20-23] to undergo dimerization within the temperature range 225 to 500°C and at higher temperature it decomposes by two different reactions[24,25] (Eqs (*B*) and (*C*)).

$$2\,CH_2{=}C{=}O \rightarrow CO_2 + CH_2{=}C{=}CH_2 \qquad (B)$$

$$2\,CH_2{=}C{=}O \rightarrow 2\,CO + C_2H_4 \qquad (C)$$

The product of dimerization, diketene, thermally decomposes[26] mainly to carbon dioxide and allene. However, these compounds were not found in the reaction mixture. The amount of carbon monoxide formed may indicate that ketene arises in the acetone–SF_6 mixture transiently and undergoes subsequent decomposition as described by Eq. (*C*). The irradiation of the ketone–SF_6 mixtures of a variable com-

TABLE I

The CO_2 Laser-Induced Decomposition of 2,3-Butanedione

Reactants (kPa)	Irradiation time s	Conversion %	Products (kPa)
$C_4H_6O_2$ (2) SF_6 (1·3)	10	62	CO, CH_4 (0·7), C_2H_2 (0·03), CH_2CO (traces)
	40	82	CO (3·3) CH_4 (0·9), C_2H_2 (0·05)
$C_4H_6O_2$ (1·3) SF_6 (1·3)	6	64	CO, CH_4 (0·7), C_2H_2 (0·05), CH_2CO (traces)
	60	93	CO (2·4), CH_4 (1·2), C_2H_2 (1·1)

ponent ratio (acetone: SF_6 = 0·17 – 1·0, total pressure 2–4·4 kPa) revealed that the conversion of the acetone decomposition and the amount of ethylene among the products increases with the increasing amount of sulphur hexafluoride. The formation of acetylene appears interesting. The final amounts of ethylene and acetylene are smaller than expected if only these and other detected products would be formed. It therefore turns out that also other, higher-molecular weight compounds could be formed by polymerization of transient unsaturated species whose occurrence by the IR technique could not be detected.

2,3-*Butanedione*

The thermal decomposition of 2,3-butanedione[13–16] (240–630°C, <0·1 – 100 kPa) proceeds by a radical mechanism and yields carbon monoxide, methane, ketene and acetone. The ketene formed undergoes subsequent decomposition and polymerization. The similar reaction course can be also ascribed to the LPHP of 2,3-butanedione performed in the presence of sulphur hexafluoride (Table I) studied with the laser output of 18 W for two different 2,3-butanedione/SF_6 initial ratios. Besides the conventional pyrolytic products acetylene is also formed. Unexpectedly small amounts of methane and the surprisingly formed acetylene would be consistent with polymerization of transiently formed unsaturated fragments.

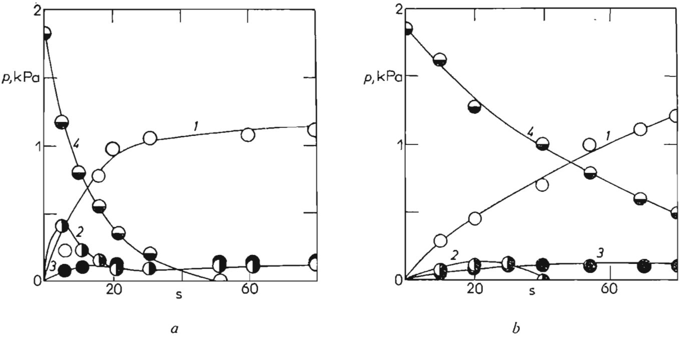


FIG. 2

The Dependence of the Product Composition on the Irradiation Time (*1* ethylene, *2* ketene, *3* acetic acid) for the Decomposition of Cyclobutanone (*4* 1·9 kPa) Induced by the CO_2 Laser Irradiation in the Presence of SF_6 (1·3 kPa)

a Laser output 18 W; *b* Laser output 8 W.

Cyclobutanone

The interaction of the CO_2 laser radiation with the mixture of cyclobutanone (1·9 kPa) and sulphur hexafluoride (1·3 kPa) leads to a mixture of products whose composition is dependent upon the laser output. With the laser output 18 W cyclobutanone affords following compounds (in parentheses partial pressure of a compound in kPa at the end of the experiment (8 s of irradiation) is given): ethylene (1·1), ketene (0·04), carbon monoxide, acetic acid (0·04) and acetylene (0·05). The irradiation of the same mixture by the laser beam of the output 8 W gives rise to ethylene (2·8), ketene (0), acetic acid (0·03) and carbon monoxide. The thermal decomposition of cyclobutanone[17-19] studied within the range of 330–410°C and 0·6–100 kPa is a molecular process occurring according to Eqs (*D*) and (*E*).

TABLE II

The Half-Time, $\tau_{1/2}$ of the CO_2 Laser Induced Decompositions of 2,3-Butanedione

Reactants kPa	Laser output W	$\tau_{1/2}$ s
C_4H_6O (2), SF_6 (1·3)	18	10
C_4H_6O (2), SF_6 (1·3)	8	45
C_4H_6O (2), SF_6 (1·3), He (1·9)	18	40

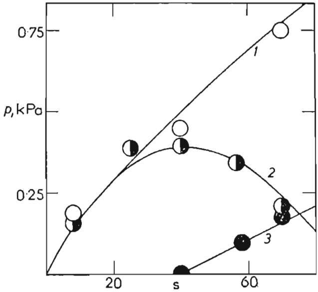
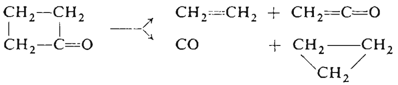


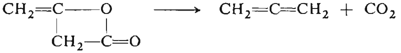
FIG. 3

The Dependence of the Product Composition on the Irradiation Time (*1* ethylene, *2* ketene, *3* acetic acid) for the Decomposition of Cyclobutanone (1·9 kPa) Induced by the CO_2 Laser Irradiation in the Presence of SF_6 (1·3 kPa) and Helium (1·9 kPa)



(*D*)
(*E*)

The reaction course of the laser-induced decomposition is different from the decomposition initiated by heat (Figs 2 and 3). The amount of ketene formed during the irradiation is by much lower than the amount of ethylene. Fig. 2 gives the reaction product composition during irradiation of the cyclobutanone–SF_6 mixtures with the laser output of 8 and 18 W. It turns out that the ketene pressure, always lower than that of ethylene, reaches its maximum after 5 s (18 W output), or 30 s (8 W output) and then decreases. The fact that the LPHP of cyclobutanone yields carbon monoxide with no traces of cyclopropane implies that ketene has to undergo the decomposition (*C*). The occurrence of acetic acid in the reaction mixture may, however, suggest that both the processes yielding carbon monoxide, *i.e.* either the decomposition of ketene (*C*) and/or the decomposition of intermediary formed diketene (*F*) are possible.



(*F*)

The formation of acetic acid by a direct reaction between ketene and water traces seems less probable, since this instant reaction would either result in the simultaneous maximum pressure of ethylene and acetic acid, or acetic acid would be formed from the very beginning of the decomposition. The latter is the case for the irradiation of the cyclobutanone–SF_6 mixture by using the laser output of 18 and 8 W (Fig. 2) when the pressure of acetic acid slowly approaches the limit value (0·03 kPa), but not for the irradiation of the mixture diluted with helium (Fig. 3). Figures 2 and 3 show that the decomposition rate is markedly influenced by the laser output and by the addition of inert buffer gas. The time interval required for 50% decomposition of cyclobutanone is for the different laser outputs and the dilution of the mixture by helium seen from Table II. As it appears, both the decrease in the laser output and the helium admixture result in the decrease of the decomposition rate. The data indicate that the laser induced decomposition of cyclobutanone is accompanied by decomposition of ketene and by obviously radical reactions yielding acetic acid.

CONCLUSIONS

The interaction of acetone, 2,3-butanedione and cyclobutanone with the CO_2 laser radiation sensitized by sulphur hexafluoride allowed to perform the LPHP of these compounds. Besides the products of conventional pyrolysis (acetone → ketene + + methane, 2,3-butanedione → methane + ketene + carbon monoxide, cyclobutanone → ketene + ethylene) or the compounds formed by the decomposition of intermediary formed ketene this technique yields also acetylene (from acetone and 2,3-butanedione) and acetic acid (from cyclobutanone). Formation of these compounds can be explained by a partly different behaviour of radicals generated during the LPHP and those produced in conventional reactors for thermal decompositions.

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