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Molecular Decomposition of Acetone

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Abstract: *The absence of a radical-scavenging effect by [$^2H_4$]germane in ArF laser-induced photolysis of acetone at relatively high radiation fluences is consistent with molecular expulsion of ethane from acetone.*

The extensive study of the photolysis of acetone using excitation via electronic absorption bands at 290[1a-d], 200[1e-i], and 147 and 129[1j] nm revealed that the major decomposition pathway is formation of two methyl radicals and carbon monoxide, which occurs via a two step mechanism[1f,g] (eq.1); minor processes are[1h-j] cleavages into H· + ·CH_2COCH_3 and CH_4 + CH_2CO both of which seem to be facilitated[1a,b] at lower wavelengths.

$$CH_3COCH_3 \longrightarrow CH_3CO\cdot + CH_3\cdot \longrightarrow 2\ CH_3\cdot + CO \qquad (1)$$

The occurrence of the transient H·, CH_3· and CH_3CO· species had been proved earlier by scavenging experiments and recently in flash- and laser-induced photolysis experiments by time-resolved techniques[1d,h,i]. The final products ethane and carbon monoxide can in principle also be formed by a molecular expulsion, but this mechanism has not been detected previously, and has been assumed to occur only as a negligible pathway[1a,e].

We now report the first evidence on a molecular cleavage of acetone into ethane and carbon monoxide and show that this mode of decomposition is dominant when acetone is ArF laser-irradiated with considerably higher fluences than in previous studies[1h,i]. [$^2H_4$]Germane, which does not absorb[2] at 193.3 nm and which can be considered[3] as an efficient scavenger of radicals, was used as a probe for a radical mechanism. Acetone (2.7 - 2.8 kPa) and the mixture of acetone (2.3 kPa) with [$^2H_4$]germane (4 kPa) were irradiated using an ArF (a Questek series 2000) laser operating at 193.3 nm (energy fluence 70 mJ.cm^{-2}, FWHM 15 ns and repetition frequency 20 Hz) in a glass reactor[4] furnished with two NaCl and two quartz (orthogonally positioned) windows and a side-arm for a withdrawal of samples for GC analysis. The acetone/[$^2H_4$]germane mixture was also irradiated by a mercury lamp to prove the scavenging ability of [$^2H_4$]germane for CH_3· radicals.

The progress of the laser photolysis, monitored directly in the reactor by FTIR spectroscopy[5] and also by g.l.c.,revealed that the major products are ethane, carbon monoxide and methane together with very small amounts (5 times or less than CH_4) of ethyne and ethene. C_2H_6, CO and CH_4, but not C_2H_2 and C_2H_4, and an almost identical photolysis progress were also observed upon laser-irradiation of the mixture of acetone with [$^2H_4$]germane (Fig.1a). The unique feature of this similarity can be understood by comparison with the progress of the mercury-lamp induced photolysis of the same mixture, which yields mostly CH_3D and small amounts of C_2H_6 and CH_4 (Fig.1b). The high yield of [$^2H_1$]methane is in line with a high efficiency of

[$^2H_4$]germane to scavenge methyl radicals via deuterium-abstraction reaction. The same course of the Ar laser-induced photolysis of acetone in the absence and presence of [$^2H_4$]germane, and the absence of [$^2H_1$]methane in the photolysis of acetone - [$^2H_4$]germane can thus be taken as a confirmation of the absence of methyl radicals and of a molecular cleavage of two methyl groups from acetone in this laser-induced reaction.

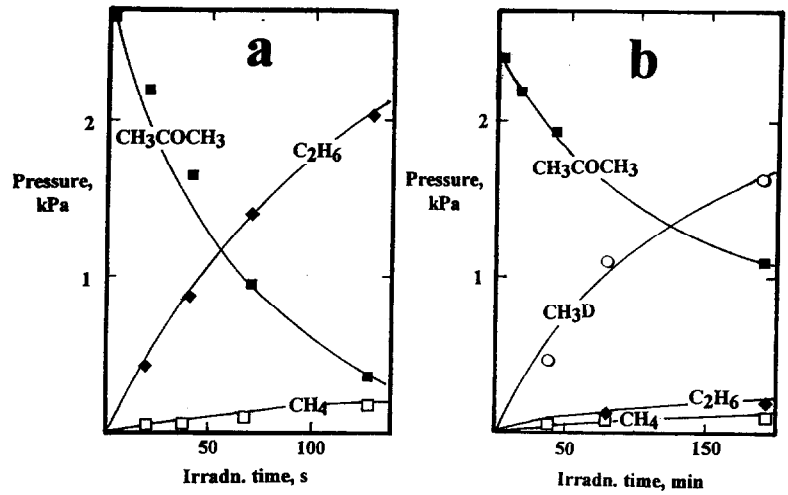

Fig. 1
ArF laser (a) and Hg lamp (b) induced photolysis of acetone in the presence of [$^2H_4$]germane.

The irradiation parameters are compatible with laser intensity ca. 2 MW. cm^{-2} and we assume that the unique molecular decomposition of acetone is a result of multiphoton excitation and of the recombination of two simultaneously generated CH_3• radicals within the molecular sphere. More work is underway to elucidate the possibilities of inducing molecular expulsion of different groups from complex organic molecules and to assess the potential of these laser photolyses for synthetic applications.

References and Notes

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5. Acetone at 1217 cm^{-1}, methane at 3016 and 1305 cm^{-1}, and [$^2H_1$]methane at 2199 and 1157 cm^{-1}.

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