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Infrared Laser-induced Decomposition of *tert*-Butyl Alcohol

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The decomposition of *tert*-butyl alcohol (2-methylpropan-2-ol) by pulsed infrared radiation from a TEA CO_2 laser has been examined, using the 10P30 line at 934.9 cm^{-1}. Over the pressure range 0.007–1.3 kPa the absorption cross-section increases with increasing pressure due to hole-filling by collisional rotational relaxation. Experiments on the decomposition were carried out at low total pressure (6.7 Pa) to minimise the effects of collisions during the pulse. The fluence range used was 3.3–6.4 J cm^{-2}. Under these conditions the only decomposition product detected was isobutene (2-methylpropene) generated in the reaction:

$$(CH_3)_3COH \longrightarrow (CH_3)_2C{=}CH_2 + H_2O$$

Addition of the diluent gases hexane and xenon reduced the extent of decomposition, and product yields from the diluted *tert*-butyl alcohol were compared with values calculated by assuming particular forms of the intermolecular energy distribution and by using RRKM rate constants. The comparison indicates that about half the irradiated molecules absorb the 10P30 radiation. The fraction of absorbing molecules deduced from the absorption measurements is considerably smaller than this, and reasons for the discrepancy are discussed.

Infrared multiple photon absorption and the resultant unimolecular decomposition of molecules in the gas phase continues to attract attention,[1–5] following several years of extensive study.[6] In previous work[7,8] we have examined the infrared laser-induced decomposition of 2,2-dimethyloxetane and of 2-methyloxetane, and attempted to link the energy absorbed by these molecules to the extent of decomposition. A feature of these experiments was the use of oxetanes diluted with an excess of inert gas to minimise thermal reaction after the excitation, and the use of low pressures to achieve essentially collision-free excitation. For both of the oxetanes it was necessary to assume that a large fraction, but not all, of the irradiated molecules absorbed the radiation, in order to reconcile the absorption and decomposition measurements. We have now carried out work on the infrared absorption and decomposition of *tert*-butyl alcohol, a molecule whose thermal decomposition has been widely studied.[9–12] Although there is some free-radical participation in the thermolysis at low temperatures,[11] the principal reaction in the shock tube at *ca.* 1000 K is molecular dehydration:[9,10]

$$(CH_3)_3COH \rightarrow (CH_3)_2C{=}CH_2 + H_2O \qquad (1)$$

In the present work we have carried out measurements of the absorption by *tert*-butyl alcohol of 10P30 radiation from a pulsed CO_2 laser. The consequent decomposition of the alkanol, both alone and when diluted with inert bath gases, has been monitored. As in previous work,[7,8] RRKM calculations have been carried out to relate absorption and decomposition.

Experimental

The experimental procedure used has been described previously.[7] The gaseous alkanol was contained in a cell of length 80 mm and internal diameter 20 mm fitted with NaCl windows. A parallel beam of pulsed infrared radiation from a TEA CO_2 laser passed centrally through the cell. Incident and transmitted pulse energies were measured using beam splitters and calibrated joulemeters, and measurements of small absorbed energies were carried out optoacoustically. The beam had a Gaussian profile of radius 0.78 mm at the point where the intensity was e^{-1} times the peak value. A deconvolution procedure[13] was used to convert results to those corresponding to a beam of uniform fluence for comparison with model calculations. All experiments were carried out with the 10P30 line at 934.9 cm^{-1}.

Isobutene and other decomposition products were collected from repetitive pulsing at *ca.* 2 Hz and measured gas chromatographically. AnalaR *tert*-butyl alcohol (BDH) was used without further purification.

Results and Discussion

Reaction Products

The major decomposition product observed under all experimental conditions was isobutene from reaction (1).

Yields of isobutene, expressed as *Y*, the fraction of *tert*-butyl alcohol molecules within the irradiated volume producing C_4H_8 per laser pulse, are shown as a function of pressure in Fig. 1. For a fixed value of fluence, the yields vary little with pressure in the range 0.03–0.8 Torr.† The minor products CH_4, CO, H_2, C_2H_4, C_2H_6 and C_2H_2 were observed in some experiments. These decreased in importance relative to isobutene as the pressure was lowered, and were detected only at the highest fluences used and at pressures above *ca.* 1 Torr, where they constituted less than 1% of the products.

Absorption Measurement

The effect of pressure on the absorption cross-section of *tert*-butyl alcohol for pulsed 10P30 radiation was examined for a fluence of 5.9 J cm^{-2}. The results showed that at 50 mTorr and below the cross-section was equal to 3.5×10^{-20} cm^2 $molecule^{-1}$ and that at higher pressures it increased. The cross-section rose from 3.7×10^{-20} cm^2 $molecule^{-1}$ at 0.1 Torr to 8.8×10^{-20} cm^2 $molecule^{-1}$ at 1 Torr and 15.9×10^{-20} cm^2 $molecule^{-1}$ at 5 Torr (all values are raw data, not deconvoluted). Above 5 Torr there was a further small increase in the cross-section to 17.1×10^{-20} cm^2 $molecule^{-1}$ at a pressure of 10 Torr. At pressures of 50 m Torr and below the interval between collisions is sufficiently

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† 1 Torr = (101 325/760) Pa.

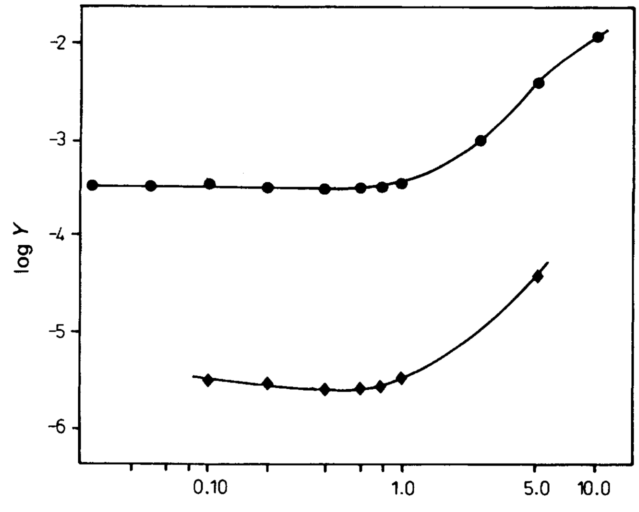

Fig. 1 Yields of isobutene from the decomposition of *tert*-butyl alcohol. Not deconvoluted. ●, Fluence = 5.9 J cm^{-2}; ◆, fluence = 3.4 J cm^{-2}

large for the effect of collisions during the pulse to be negligible. Under these circumstances molecules not in appropriate vibrational–rotational states for absorption remain unexcited, whereas at higher pressures some are transferred into absorbing states by collisional rotational relaxation during the pulse. Further experiments on absorption and decomposition either of pure *tert*-butyl alcohol or of *tert*-butyl alcohol diluted with other gases, were carried out at a total pressure of 50 mTorr to ensure effectively 'collision-free' excitation.

Over the fluence range examined experimentally there was a linear dependence of the number of 10P30 photons absorbed under 'collision-free' conditions on the laser fluence. This dependence, shown in Fig. 2, implies a slight decrease of the absorption cross-section with increasing fluence, by 6% over the range 3.4–5.9 J cm^{-2}.

Decomposition Yields

The extent of decomposition of *tert*-butyl alcohol, expressed as Y, the fraction of the molecules in the irradiated volume decomposed per laser pulse, was measured at different fluences for 'collision-free' excitation at a pressure of 50 mTorr. The results are shown in Fig. 3. Decomposition of the pure alkanol in these circumstances is due partly to the decomposition of laser-excited molecules before any collisions occur, and partly to thermal and quasi-thermal decomposition occurring after redistribution of energy between molecules as a result of collisions. The extent of thermal decomposition is difficult to estimate.[14,15] In order to eliminate this uncertain component of the product yield, experiments were carried out on the decomposition of *tert*-butyl alcohol diluted with an excess of inert gas. The total pressure was kept at 50 mTorr, 5 mTorr *tert*-butyl alcohol with 45 mTorr inert gas, to maintain essentially collisionless excitation.

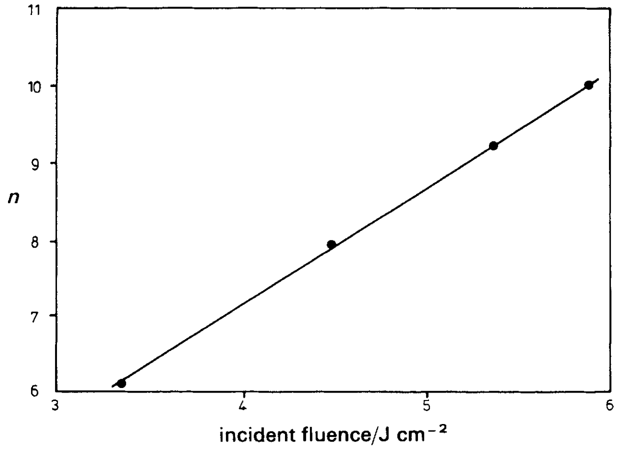

Fig. 2 Variation of number of absorbed photons per molecule (n) with fluence for 50 mTorr *tert*-butyl alcohol. Deconvoluted values. 10P30 line

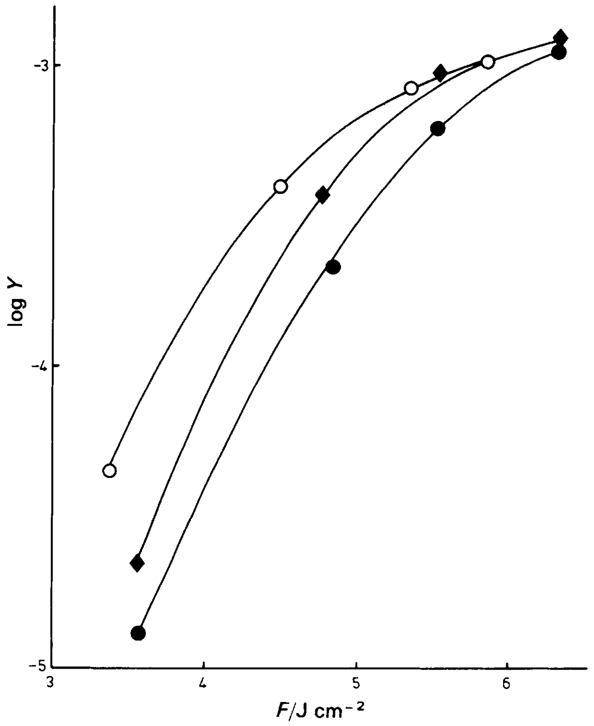

Fig. 3 Variation of decomposition of *tert*-butyl alcohol with fluence. Deconvoluted values. ○, 50 mTorr *tert*-butyl alcohol; ●, 5 mTorr *tert*-butyl alcohol plus 45 mTorr hexane; ◆, 5 mTorr *tert*-butyl alcohol plus 45 mTorr xenon

Results of experiments using the diluents hexane and xenon are compared with those for pure *tert*-butyl alcohol in Fig. 3. As a consequence of the low pressures the absorption cross-section for *tert*-butyl alcohol in the dilute mixtures is expected to be equal to that of the pure material. The effect of adding hexane is to reduce the decomposition significantly, particularly at the lowest fluence. This implies that in pure *tert*-butyl alcohol there is an important contribution of post-pulse thermal decomposition to the product yield at low fluences. A similar effect is observed in the laser-induced decomposition of 2,2-dimethyloxetane[7] and of 2-methyloxetane.[8] As would be expected, added xenon also reduces the decomposition, but less effectively than hexane.

Calculated Decomposition Yields

As a first step in examining the extent of decomposition, calculations of hypothetical decomposition yields for the mixtures of *tert*-butyl alcohol with an excess of bath gas, hexane or xenon, were carried out. The use of the dilute mixtures avoids the problem of the estimation of the extent of thermal decomposition which, as can be seen from Fig. 3, may be considerable. In calculating the hypothetical yields two particular forms of intermolecular energy distribution for the *tert*-butyl alcohol molecules were assumed. The energy absorbed from the laser pulse, plus the initial vibrational energy of the molecules before absorption, was taken to be distributed as vibrational energy among all the irradiated *tert*-butyl alcohol molecules according to either a Poisson or a Boltzmann distribution. Fractional decomposition yields were then calculated by using specific rate constants $k_a(E_v^*)$ together with step-ladder deactivation with step sizes of 20.9 kJ mol^{-1} for collisions of *tert*-butyl alcohol with hexane and 8.4 kJ mol^{-1} for collisions with xenon.

Specific rate constants $k_a(E_v^*)$ were calculated from conventional RRKM theory.[16] The molecule frequencies used in the calculations were those of ref. 12. It was assumed that in forming the activated complex for elimination of water, one CH stretching frequency, one of the methyl deformation frequencies, the CO vibration frequencies and the skeletal vibration frequencies would be most affected. Accordingly those frequences marked with an asterisk in Table 1 were systematically adjusted until agreement was obtained with the experimental Arrhenius *A* factors.[9–12] The reaction coordinate was taken to be the C—C—C bending vibration at 424 cm^{-1}.[17] The frequencies taken for the activated complex and other parameters used in the RRKM calculations are shown in Table 1.

Calculated product yields corresponding to any particular laser fluence, based on the assumption that the absorbed energy is distributed among all the molecules in the irradiated volume, were much lower than the corresponding experimental values, whether a Boltzmann or Poisson intermolecular distribution was assumed. For example, on the assumption of a Poisson distribution, calculated decomposition yields of *tert*-butyl alcohol diluted with a nine-fold excess of hexane are 1.25×10^{-11}, 1.35×10^{-9}, 1.06×10^{-8} and 8.98×10^{-8} for fluences of 3.55, 4.84, 5.52 and 6.33 J cm^{-2}, compared with experimental yields of 1.28×10^{-5}, 2.17×10^{-4}, 6.28×10^{-4} and 1.13×10^{-3}, respectively. Calculated yields for the Boltzmann distribution, while higher than these values, are still far below the experimental fractional decompositions. The reason for the discrepancy is that for collisionless excitation some molecules in the irradiated volume are in initial vibrational rotational states that are unfavourable for multiple photon absorption and remain unexcited or absorb only weakly. The absorbed energy is consequently distributed between fewer molecules than assumed in the calculation and the extent of decomposition of the absorbing molecules is increased.

The actual intermolecular energy distribution produced by irradiation, including the unexcited and weakly excited molecules, is complex. Rough estimates of the proportion of 'cold' molecules can be obtained by making arbitrary assumptions about the distribution. In the simplest of these, the molecules are divided into two groups, those which absorb no energy from the laser radiation and those which do absorb, the intermolecular energy distribution of the latter group being assumed to be either Boltzmann or Poisson. The fraction of the molecules which absorb laser radiation, *q*, can then be evaluated by finding the value which is required to give agreement between calculated and experimental decomposition yields. Application of this procedure to the experimental results gave similar values of *q* for *tert*-butyl alcohol diluted with hexane and with xenon. In the fluence range 3.5–6.3 J cm^{-2} the calculated values of *q*, the fraction of irradiated molecules interacting with the laser radiation, were *ca.* 0.5 for an assumed Poisson distribution and *ca.* 0.6 for an assumed Boltzmann distribution and increased slightly with increasing fluence. Such calculations oversimplify the situation, but the results clearly point to a degree of selective excitation among the irradiated molecules.

Table 1 Parameters used in RRKM calculations

vibrational wavenumbers/cm^{-1}	
molecule[12]	activated complex
3643, 2980 (6), 2910 (2)*, 2880* 1472 (5)*, 1450, 1395, 1374 (2), 1330	as for the molecule except those with asterisk replaced by 2910 (3), 1487.3 (2), 1472 (3)
1230*, 1215, 1140, 1106 (2)*, 1013 (3)	1242.8, 1117.5, 1106, 755.8
919, 748*, 462 (2), 424, 356, 344	272.8, 270 (2), 201,
270 (3)*, 200*	and 424 dropped to become the reaction coordinate; $\log(A/s^{-1}) = 14.02$;
	critical energy = 267.8 kJ mol^{-1}
	reaction-path degeneracy = 9

Fraction of Absorbing Molecules

It is interesting to compare these results with the absorption measurements described earlier. The increase in absorption with pressure was attributed to the collisional transfer of non-absorbing molecules to absorbing states. A simple interpretation of this effect identifies *q* with the ratio of the measured absorption cross-section at low pressure to that at very high pressure, when it is assumed that all non-absorbing molecules are brought into absorbing states by collisions during the pulse. Taking the high-pressure limit of the absorption cross-section of *tert*-butyl alcohol for 10P30 radiation (5.9 J cm^{-2}) as *ca.* 18×10^{-20} cm^{-2} molecule^{-1}, the value of *q* calculated in this way is 0.19, much lower than that inferred from the decomposition yields. A similar discrepancy can be seen in the case of 2-methyloxetane.[8]

The difference may be due in part to experimental and computational uncertainties in the measurement of yields, the deconvolution procedure and the RRKM calculations, and in the use of absorption cross-sections calculated from undeconvoluted results. However, a more important reason for the disagreement in the values of *q* lies in the inadequacy of the models used for each of the calculations. The division of irradiated molecules into two groups, one having absorbed no energy and the other having an arbitrarily assumed distribution, is an oversimplification of the actual intermolecular energy distribution. In addition, the effect on absorption of the collisions which occur during the pulse at higher pressures is not simply one of transferring non-absorbing molecules into states that are more suitable for absorption. Molecules which have absorbed several photons will also lose energy in collisions and be transferred to lower levels of excitation with a corresponding increase in the effective absorption cross-section. Thus the increase of cross-section with increasing pressure is not due only to rotational hole-filling, and calculations based on that assumption will tend to underestimate the value of *q*. If the idea of the fraction of molecules interacting with the radiation is retained as a useful approximate way of describing the system then the value of *q* must be put at 0.4 ± 0.2

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