IR MULTIPHOTON DECOMPOSITION OF DIMETHYL ETHER

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Summary

Multiphoton IR decomposition of $(CH_3)_2O$ yields CO which is enriched in ^{18}O. The selectivity exceeds 100 at low conversions but decreases rapidly as the reaction proceeds. This decrease is shown to be caused by depletion of ^{18}O-containing reactant molecules.

1. Introduction

This work is part of a series of continuing studies [1 - 9] on the application of multiphoton IR photolysis techniques to systems which may be useful for the preparation of compounds enriched in rare isotopes. We report an initial attempt to extend the work on ^{13}C enrichment to ^{18}O. Hexafluoroacetone decomposition is known to provide CO enriched in ^{13}C when excitation is at the red edge of the antisymmetrical C—C—C stretching vibration [2, 3]. The analogous vibration of the C—O—C group in dimethyl ether lies in a region accessible to a CO_2 laser (band head near 1120 cm^{-1} [10, 11]) so that this molecule was chosen for this initial work.

In an earlier study of this system Vizhin *et al.* [12] excited mixtures of variously labelled ethers at several frequencies in the 9.4 μm band of a transversely excited atmospheric pressure (TEA) CO_2 laser (about 0.2 J pulse^{-1}) using a focused beam (7 cm lens) and were able to demonstrate the preferential decomposition of $(^{13}CH_3)_2O$ or $(CD_3)_2O$ in mixtures with natural $(CH_3)_2O$. They used natural ether with excitation in the focused beam at the 9P16 line (1050.4 cm^{-1}) in experiments of unspecified duration and found that the ^{18}O in the residual ether had been depleted by a factor of at least 1.6. Irradiation closer to the band centre allowed identification of the products of the decomposition and this permitted them to suggest a free-radical mechanism consistent with those observations.

This early work is significant in that it demonstrated isotopically selective decomposition. However, it leaves considerable scope for improvement since only β values were measured and only strongly focused beams were used. The present work was undertaken primarily to determine whether

high intrinsic selectivities were possible for the multiphoton dissociation of ^{18}O molecules in an approximately parallel beam.

2. Experimental details

Irradiation was always performed using a beam of the P16 line (1050.4 cm^{-1}) of the 9.4 μm band from a Lumonics 103 TEA CO_2 laser which had been mildly condensed using long focal length lenses and passed through appropriate apertures. In one series of experiments (A) a cell 17.5 cm long and 5 cm in diameter was placed approximately 1 m from a lens of 2 m focal length (beam diameter, 1.3 cm; fluence, about 2.4 J cm^{-2}). Products volatile at the temperature of solid nitrogen were expanded to the inlet system of a Hitachi RMU-60 mass spectrometer for isotopic analysis of the CO. Although the use of solid nitrogen was imperative in order to eliminate the contribution of ethane to the peaks at $m/e = 28$, $m/e = 29$ and $m/e = 30$, its use precluded accurate estimates of the total amount of volatile product formed because variable amounts of the methane product were retained in the cold trap probably by adsorption on surfaces. No attempt was made to analyse other products except to identify ethane as the only major constituent volatile when the trap was warmed to -160 °C.

In a second series of experiments (B) performed many months later with different apparatus, a smaller cell 10 cm long and 1.5 cm in diameter was located approximately 100 cm from a lens of focal length 200 cm (beam diameter, 0.8 cm; fluence, 1.6 J cm^{-2}). Material volatile at -196 °C was shared with the injection volume [13] of a Finnigan OWA 1020 gas chromatograph–mass spectrometer fitted with a Porapak S (80/100 mesh) column of dimensions 6 ft by 1/8 in and operated isothermally at 60 °C for the analysis of non-condensables and at 150 °C for the condensables. The isotopic analysis of CO and methane was impractical for most experiments because of the small amount of product. The material condensed at -196 °C was also analysed and the isotopic composition of the residual ether was measured. Ethane was the only product identified with certainty in this fraction although traces of propane were detected in some experiments at higher conversions.
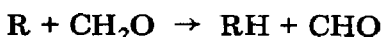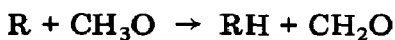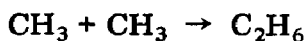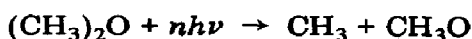
The dimethyl ether (Matheson) was used as received except for rigorous outgassing at -196 °C; traces of CO_2 impurity were detected.

3. Results and discussion

In experiments A the amount per pulse of products volatile at the temperature of solid nitrogen decreased by more than an order of magnitude as the reactant pressure increased from 0.2 to 1.5 Torr. However, it is not possible to consider this deactivation quantitatively because of the variability of the data which was probably caused by the adsorption phenomenon

noted earlier. Moreover, at a given pressure (0.50 or 0.76 Torr) the amounts of volatile product per pulse increased as the number of pulses increased. Again the adsorption phenomenon might account for some of this increase but another factor must be that one of the constituents of the mixture measured was formed in secondary reactions.

If secondary photolysis of the radicals initially formed can be neglected, the overall decomposition probably involves the following sequence of reactions [12]:

$$(CH_3)_2O + nh\nu \rightarrow CH_3 + CH_3O$$

$$CH_3 + CH_3 \rightarrow C_2H_6$$

$$R + CH_3O \rightarrow RH + CH_2O$$

$$R + CH_2O \rightarrow RH + CHO$$

$$R + CHO \rightarrow RH + CO$$

The radicals CH_3 and CH_3O are formed in the primary decomposition and R represents either of these so that RH represents methane or methanol. Some dimethyl peroxide might form by combination of methoxyl radicals but the ratio of disproportionation to combination for these radicals is reported to be large [14]. Methyl and methoxyl radicals may also recombine (the ratio of disproportionation to combination is 1:2 [14]) but such recombination merely lowers the apparent quantum efficiency of the primary decomposition.

Given the conditions of high radical concentrations in these experiments, it is improbable that a significant fraction of the primary radicals would react with the reactant ether to form methoxymethyl radicals and thence, by combination with methyl or methoxyl radicals, methyl ethyl ether or dimethoxymethane. Trace amounts of methyl ethyl ether were detected by Vizhin *et al.* [12] but none of these products was detected, nor sought specifically, in this study. Despite the high radical concentrations it is not unreasonable to expect that primary radicals could attack the formaldehyde product as the rate constant for attack by methyl radicals on formaldehyde is greater than that for attack on ether by a factor of 10^2 at room temperature [14]. An analogous argument indicates that radical attack on the methanol product should be unimportant.

Provided that neither CO nor formaldehyde undergo exchange reactions with the walls etc., the mechanism requires that the isotopic composition of the CO formed be identical with that of the formaldehyde precursor which in turn is determined by that of the methoxyl radicals formed in the primary decomposition. If any such exchange occurs, the values of the primary selectivity α_{18} where

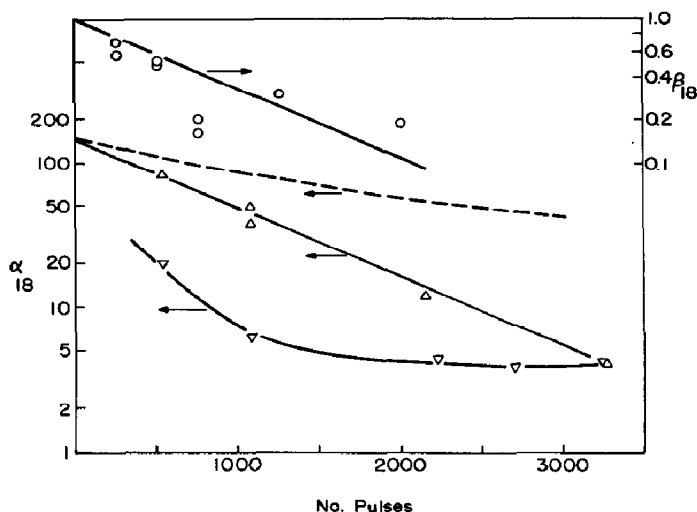$$\alpha_{18} \equiv \frac{(h_{30}/h_{28})_{obs}}{(h_{30}/h_{28})_{natural}}$$

Fig. 1. Logarithmic variation of α_{18} and β_{18} with conversion. All experiments were performed using the 9P16 line at 1050.4 cm^{-1}. Series A (2.4 J cm^{-2}): $\triangle$, [(CH$_3$)$_2$O] = 0.51 Torr; $\triangledown$, [(CH$_3$)$_2$O] = 0.76 Torr. Series B (1.6 J cm^{-2}): $\circ$, [(CH$_3$)$_2$O] = 0.48 Torr. The points are averages of two or more analyses from a single exposure; the spread of replicate analyses is included within the symbol; – – –, see text.

in the CO product, after appropriate correction for the time-dependent background, would be lower limits. Such values of α_{18} obtained from experiments in series A at two reactant pressures are shown as logarithmic functions of the conversion in Fig. 1. Also shown in Fig. 1 are values of

$$\beta_{18} \equiv \frac{(h_{48}/h_{46})_{\text{final}}}{(h_{48}/h_{46})_{\text{initial}}}$$

obtained from the residual ether in the B series of experiments.

The measured values of β_{18} decrease with conversion as expected if these are governed by

$$\beta_{18} = \frac{\{1 - {}^{18}P(v_r/v_c)\}^n}{\{1 - {}^{16}P(v_r/v_c)\}^n}$$

where v_r and v_c are the irradiated volume and the cell volume respectively, n is the number of pulses and the ${}^iP$ is the probability per pulse that an ether molecule containing isotope i is decomposed during that pulse. If the ratio ${}^{18}P/{}^{16}P$ is large, a plot of log β_{18} versus n should be linear with a slope given approximately by log $\{1 - {}^{18}P(v_r/v_c)\}$. The measured slope ($-4.8 \times 10^{-4}$ pulse^{-1}) and the measured $v_r/v_c = 0.50$ for the series B experiments yield ${}^{18}P \approx (2.2 \pm 0.5) \times 10^{-3}$ where the uncertainty is estimated from the uncertainty in the slope.

Extrapolation of the plot of log α_{18} versus n to zero conversion yields an intrinsic value ${}^{\circ}\alpha_{18} \approx 150$ which pertains to initial stages before ^{18}O depletion in the reactant ether becomes important. This ${}^{\circ}\alpha_{18}$, taken with the estimate of ${}^{18}P$, permits the estimation of ${}^{16}P = {}^{18}P/{}^{\circ}\alpha_{18} \approx 1.5 \times 10^{-5}$ thus supporting the approximation made above. It should be recalled that the

fluences used in series A and B differed so that numerical agreement cannot be expected between the values of α_{18} calculated from $°\alpha_{18}$ and ^{18}P and those measured. Indeed, the broken line shown in Fig. 1 is that calculated from the β_{18} and $°\alpha_{18}$ values; the lack of numerical agreement is evident although there is a general decline of the apparent α_{18} with conversion as observed.

The values of α_{18} obtained from the experiments at 0.76 Torr display the marked curvature anticipated if ^{18}P is much larger at this higher pressure but $°\alpha_{18}$ remains of the order of 10^2. In view of the paucity of data available at present, this suggestion of higher values of ^{18}P at higher pressure should be viewed with great caution.

It should also be noted that the ^{13}C selectivity α_{13} was relatively small in all experiments, having average values of 2.0, 2.6 and 1.8 in the products CO, methane and ethane respectively. This low selectivity for carbon is to be expected since the antisymmetrical stretching vibration should show a large isotope shift for the central atom but small shifts for terminal atoms. Thus excitation at the red edge of this band for dimethyl ether should favour ^{18}O selectivity but not be significantly selective for ^{13}C.

Finally we note that the mechanism requires that the methyl radicals released in the primary decomposition appear only in the products methane and ethane if the small fraction lost in forming methyl ethyl ether is neglected. Thus the sum $[CH_4] + 2[C_2H_6]$ measures the net number of ether molecules which decomposed and also the number of molecules containing oxygen which should appear among the CO, formaldehyde and methanol products. Although accurate quantitative analysis of the products was not attempted in these experiments, some approximate data are available which show

$$\frac{[CO]}{[CH_4] + 2[C_2H_6]} \approx 25\% \pm 5\%$$

i.e. that about a quarter of the oxygen released in the primary decomposition appears in the CO product. This value agrees with that obtained by Vizhin *et al.* [12]. Most of the balance of the oxygen would appear in the methanol product which could be recovered readily using proper techniques.

In conclusion we have demonstrated that multiphoton IR dissociation of 0.5 Torr dimethyl ether with the 9P16 line of the CO_2 laser at 1050.4 cm^{-1} at 2.4 J cm^{-2} is isotopically selective for ^{18}O. The initial selectivity is high (about 150) and the reaction can be carried to over 90% depletion without degrading this. The ^{18}O reaction probability under these conditions is acceptably high ($^{18}P \approx 2 \times 10^{-3}$). The oxygen is believed to appear in two major products, CO, which was analysed in this study, and methanol. There is no reason to expect the selectivity in the methanol product to be degraded unless exchange of oxygen atoms with the cell wall occurs. Therefore this system must be regarded as an extremely strong candidate for practical scale oxygen isotope enrichment schemes. Further work will be directed towards scaling the system to higher working pressures and to measurements of the photon efficiency of the process.

Acknowledgment

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