Laser-powered Homogeneous and Heterogeneous Pyrolysis of 2-Nitropropane

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The pyrolysis of 2-nitropropane has been studied under both homogeneous conditions (using a continuous-wave CO_2 laser and sensitized by sulphur hexafluoride) and heterogeneous conditions (pulsed pyrolysis) at temperatures in the range 820–1210 K. A comparison of both decompositions is aided by the determination of spatial temperature profiles and the effective temperature in the laser-driven reaction by using calculations of the temperature distribution, thermocouple techniques and elimination of ethyl acetate as a 'chemical thermometer'. The main process in the laser-driven decomposition is the clean decomposition into propene and nitrous acid occurring via C—N bond fission. In heterogeneous pyrolysis additional products such as 2-nitropropene, acetonitrile and acetone are formed. The high yield of 2-nitropropene at 820 K indicates a unique route to this compound.

The gas-phase thermal decomposition of 2-nitropropane as a representative of the nitroalkanes at temperatures from 513 to 1403 K has been studied intensively by static,¹⁻³ dynamic,^{4,5} very-low-pressure⁶ and shock-wave-induced⁷ pyrolysis techniques for both practical and theoretical reasons.8,9 A detailed study of the product distribution performed only over a rather narrow temperature range (523–610 K) revealed² the reaction to proceed via two competitive¹⁰ processes, namely HONO molecular elimination and C-N bond fission to form propylene and nitrous acid, followed by a series of secondary processes initiated by the attack of the decomposition products of nitrous acid on the parent molecule. The secondary processes were, based on a comparison of the rates and product distributions in reactors with different surface-to-volume ratios, inferred partly to be heterogeneous, but the effect of the reaction-vessel wall upon the product distribution has not yet been studied using more sophisticated techniques. The recently developed technique of laser-powered homogeneous pyrolysis^{11,12} completely obviates the effect of hot reactor walls and ensures that the gas-phase decomposition of an organic compound can occur without heterogeneous reaction stages. In the present investigation this technique, along with surface pyrolysis in a micropulse reactor, is applied to the decomposition of 2-nitropropane in order to determine surface effects on the distribution of the decomposition products at temperatures higher than those previously chosen.

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EXPERIMENTAL

A continuous-wave CO₂ laser with NaCl Brewster windows and grating-wavelength tuning, operating at the P(34) line of the $00^{\circ}1 \rightarrow 10^{\circ}0$ transition (931 cm⁻¹) with 5-8 W output and 0.8 cm beam diameter, was used for the irradiation experiments. The unimolecular decomposition of ethyl acetate (EA) was chosen as the reference reaction. To provide identical thermal conditions for the systems to be compared, *i.e.* the laser-photosensitized decomposition of 2-nitropropane (2NP) and that of EA, equal quantities of the reactant (2NP or EA) and SF_{e} sensitizer with or without a diluent (helium or argon), ensuring rapid thermalization,¹³ were separately irradiated using laser power with amplitude stability of $\pm 1.5\%$ (quartz-stabilized laser cavity) in an identical cylindrical glass (Simax) cell of 10 cm path length and 3.6 cm inner diameter fitted with NaCl windows and one PTFE stopcock. The laser beam was focussed (Ge lens, focal length 25 cm) at the centre of the vertically positioned cell and entered from below. The laser output was measured using a Coherent model 201 power meter, and the laser line used for irradiation was verified with a model 16-A spectrum analyser (Optical Eng. Co.). The same cell filled with a $2NP+SF_6$ mixture equipped with six or less thermocouples (jacket diameter 0.15 mm, VEB Walzwerk Hettstadt) was used for temperature measurements. The thermocouples were placed 12, 38, 63 and 88 mm (x) above the entrance window at different distances (r = 0-18 mm) from the laser beam passing through the cell along its symmetry axis. The points in space at which the thermocouple measurements were made are given as circles in fig. 2 (see later). Exact adjustment of the path of the continuous-wave CO₂ laser beam was made by matching with a visible He-Ne laser (model HNA 50, Carl Zeiss, Jena). The cells were separately attached to the apparatus as shown in fig. 1. The samples for laser irradiation were prepared by a standard vacuum-line technique and the concentrations of the individual components were checked by measuring the i.r. spectra at 1524 (2NP), 1047 (EA) and 987 (SF₆) cm⁻¹ on a Perkin-Elmer model 621 i.r. spectrometer. The absorption coefficients were ascertained by measuring the spectra of the pure samples.

The progress of the reaction with gaseous mixtures irradiated at measured intervals was monitored using a sampling valve¹³ coupled with a Chrom 3 gas chromatograph provided with flame ionization and thermal conductivity detectors and a temperature programming facility.

A thermocouple method of measuring the temperature inside the cell enabled the voltage on the individual thermocouples to be recorded at a rate of 10 channels per second by means of a digital data logger microscan (Dynamco Systems, Chertsey) with an accuracy of 0.05 mV. The results were fed onto punched paper tape and evaluated by an EC 1033 computer.

The micropulse reactor used was similar to that described in ref. (15) and consisted of a $18 \text{ cm} \times 0.2 \text{ cm}$ i.d. electrically heated stainless-steel tube, closed at one end by a silicone-rubber septum and at the other end attached to the injection port of the gas chromatograph (Chrom-3). The carrier gas was nitrogen and its flow rate was allowed to settle to obtain a suitable residence time. The temperature profile inside the middle 12 cm of the reactor was steady to within $\pm 3 \text{ K}$.

The gas-chromatographic analysis of the decomposition of 2NP and EA was carried out on 25% squalane on Chromosorb (90/105 mesh; carrier gas nitrogen; separation of 2NP, 2-nitropropene, acetonitrile, acetone, propene and methane; separation of ethyl acetate and ethylene) and on Porapak N (80/100 mesh; carrier gas hydrogen; separation of propene, nitrous oxides, nitric oxide and water).

For the identification of the decomposition products both the comparison of their retention time with that of a standard compound and the g.c./m.s. system were used. The latter consisted of a Pye–Unicam 104 gas chromatograph equipped with a packed column ($3 \text{ m} \times 3 \text{ mm i.d.}$, 10% OVE 17 silicone elastomer on Chromosorb W-DMCS) connected to an AEI MS 902 double-focussing mass spectrometer (Associated Electric Industries, Manchester) by means of a steel capillary and a Watson–Biemann separator. The quantitative analysis was done by peak-area measurements, taking into account detector response factors.

Sulphur hexafluoride (Montedison Milano, I.E.C. standard) and ethyl acetate (Lachema, Brno) were commercial products. 2-Nitropropane was obtained by treatment of 2-bromopropane with sodium nitrite, a procedure similar to the preparation of 2-nitro-octane.¹⁶ The yield of 2NP (at 65 °C) depended upon the reaction conditions (solvent, reaction time) and was 0% (dimethylformamide, 13 h), 4.5% (dimethylsulphoxide, 4 h) and 11% (hexamethylphosphotriamide, 5 h).

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Fig. 1. Apparatus used for the laser-driven pyrolysis of 2NP and the measurement of temperature distribution. a, CO_2 laser; b, He-Ne laser; c, rectangular NaCl window; d, revolving chromium coated mirror; e, Coherent model 201 powermeter; f, reaction cell (f_1) or cell for measurement of temperature (f_2); g, thermocouples; h, reference cell for i.r. analysis; i, vacuum line; j, digital centre; k, computer; l, sampling valve; m, gas chromatograph; n, i.r. spectrometer.

The computer program developed for the estimation of the temperature throughout the cell in the laser experiments as a function of the cell radius (r) and length (x) was similar to that described in ref. (17), where a steady-state temperature distribution, insignificant convection, thermal conductivity being dependent on temperature, and monotonic dependence of laserbeam absorption on pathlength were assumed. In our program the absorption of the laser beam was considered to be controlled for the relatively high concentration of SF₆ used in our experiments by the Beer-Lambert law. Moreover, except for argon and helium,¹⁸ the thermal conductivity was assumed to be independent of temperature (the value at 300 K for SF₆ diluent systems was equal to that of pure diluent).

RESULTS AND DISCUSSION

Chemical reactions induced with a c.w. CO_2 laser are generally assumed to proceed far from the reactor walls and to have a non-uniform temperature distribution. In reviewing the previously described methods for evaluation of thermal and/or kinetic parameters, three approaches must be considered. Convection being unimportant, the rate constant and translational temperature at a given position of a reactor can be obtained^{17, 19} through a series of special procedures based on measurements of laser-induced reaction rate and optical absorption which include interferometric measurements of temperature. The temperature can also be measured directly using probes as thermocouples,²⁰ but this may introduce errors in regions of large temperature gradients and inside the beam region. Provided that convection times are rapid relative to the reaction rate a practical procedure can be applied, either treating the reacting system as though it were characterised by a mean effective temperature throughout the reactor volume¹¹ or assuming non-isothermal conditions in the form of a parabolic temperature distribution²¹ in a limited reactor space (the so-called 'hot-zone').

In the present investigation the temperature distribution was measured by means of a thermocouple technique. The vertically positioned tube-like cell reactor was

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Fig. 2. Temperature distribution inside the cell (r = 18 mm, x = 100 mm) after 3 s irradiation of the 2NP (1.7 kPa) + SF₆ (0.7 kPa) mixture with the focussed laser beam [P(34) line, 6 W output].

irradiated at its centre from the lower window; in such a case the temperature distribution was found to be symmetrical along the laser beam. The temperature profiles acquired for the $2NP + SF_6$ mixture (fig. 2) irradiated with the laser beam at 6 W output after 3 s exposition (a time at which 2NP decomposition had already progressed to a pronounced conversion and a steady temperature state had been achieved) are extrapolated (fig. 2, dashed curve) by consulting the computed temperature profiles for laser-irradiated sulphur hexafluoride and its mixtures with argon or helium (fig. 3). The difference in character between the experimental (fig. 2) and calculated (fig. 3) temperature distributions supports the importance of convection currents neglected in the calculation. Maximum temperatures in the SF_6 , SF_6 + Ar and SF_6 + He systems computed for thermal conductivity independent of temperature decrease in the above order, taking the values 4407, 2578 and 547 K. Lower values of T_{max} for SF₆ + Ar and SF₆ + He were computed when the thermal conductivity was assumed to be dependent on temperature, and are 1391 and 520 K, respectively. These latter values are certainly more realistic, T_{max} for the SF₆ + Ar system being reasonably higher than the mean effective temperature for this system obtained from kinetic data on the decomposition of 2NP and EA (table 1).

The laser-photosensitized decomposition of 2NP yields propene, nitrogen oxides, water and methane and is strongly influenced by the cleanliness of the cell windows and the configuration (vertical or horizontal) of the irradiated cell. Contamination of the entrance window by dust or dirt, and to a lesser extent a horizontal cell configuration, facilitates the formation of additional compounds, acetone and acetonitrile. Their yield diminished upon careful cleaning of the cell windows and did not increase even when the laser output was increased from 5 to 8 W. By analogy with other examples of laser-induced surface-catalysed reactions^{23–25} the production of acetone and acetonitrile can be accounted for by the direct heating of the cell window and by convection currents bringing hot molecules onto the cell wall.

Under conditions which do not permit surface chemistry the progress of the reaction and mass balance performed by gas chromatography coupled with sampling via a valve



Fig. 3. Temperature distribution for (a) $SF_6(1.3 \text{ kPa})(T_{\text{max}} = 4407 \text{ K}), (b) SF_6(1.3 \text{ kPa}) + \text{argon}, (T_{\text{max}} = 2578 \text{ K}) \text{ and } (c) SF_6(1.3 \text{ kPa}) + \text{helium } (T_{\text{max}} = 547 \text{ K}) \text{ computed for the cell with } r = 18 \text{ mm and } x = 100 \text{ mm}, \text{ wall temperature 300 K}, \text{ irradiance } 0.3 \text{ W mm}^{-2}, \text{ beam radius } 1 \text{ mm}.$ The thermal conductivity was taken to be independent of temperature and the excess of diluent was sufficient to consider the thermal conductivity of the mixtures to be equal to that of the pure diluent.

	$\langle T angle^a / \mathbf{K}$					
mode	$\log_{(A \text{ s}^{-1})}$	$E / kcal mol^{-1}$	T/K	ref.	reactant $+ SF_6$	$\begin{array}{c} \text{reactant} \\ + \text{SF}_6 \\ + \text{Ar} \end{array}$
partly heterogeneous reaction ^b	11.3	40	523-1100	2,22	910	1000
five-centre molecular elimination of HONO ^e	11.5	42	ca. < 700	10	760	840
C—N bond fission ^{c}	17.5	62	<i>ca.</i> > 700	10	710	680

Table 1. Mean effective temperature, $\langle T \rangle$, estimated for different modes of 2NP
decomposition

^a Values of $\langle T \rangle = (E_{\rm EA} - E_{\rm 2NP})/\{2.3R [(\log k_{\rm 2NP}/\log k_{\rm EA}) - \log (A_{\rm 2NP}/A_{\rm EA})]\}$ where log $(A/s^{-1}) = 12.6$ and $E/kcal \, {\rm mol}^{-1} = 48$ for EA decomposition via the six-centre molecular elimination of CH₃CO₂H obtained in the temperature range 725–883 K were taken from ref. (22). ^b Experimental. ^c Calculated using thermochemistry and estimated activation energy for the reverse reaction.

and based on the determination of absolute amounts of 2NP, propene and methane revealed that 2NP, yielding nitrogen oxides and water, completely decomposes into propene, which in turn partly (3-6%) undergoes decomposition to yield methane. Water, not detectable by g.c., was found to be absorbed on NaCl windows by i.r. spectroscopy as a weak absorption band at 1640 and 3400 cm^{-1.26}

The laser-induced decomposition apparently occurs in a cylindrical volume with an axis identical to that of the reactor and positioned between the entrance window and x = 12 mm, its diameter being less than 8 mm. This assumption is consistent with the observation of almost 70% absorption of the laser-beam energy after passage through

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Fig. 4. Dependence of the 2NP and EA decomposition progress upon time for the systems $2NP+SF_6(\bullet)$, $2NP+SF_6+Ar(\bigcirc)$, $2NP+SF_6+He(\blacktriangle)$, $EA+SF_6(\times)$ and $EA+SF_6+Ar(\bigcirc)$. The curves relate to a laser output of 6 W and reactant (1.3 kPa)+SF_6 (2.1 kPa) or reactant (1.3 kPa)+SF_6 (2.1 kPa)+diluent (36.6 kPa) mixtures.

	products ^b					
T/K	CH ₃ C(O)CH ₃	CH ₃ CHO	CH ₃ CN	CH ₃ C(NO) ₂ =CH ₂		
695						
820	0.59		0.80	2.3		
850	0.14	0.05	0.23	0.96		
870	0.05	0.03	0.09	0.58		
910	0.03	0.03	0.04	0.10		
930	0.03	0.05	0.02	0.02		
1010	0.01	0.03	0.02			
1030	0.03	0.06	0.02			

Table 2. Heterogeneous pulsed pyrolysis^a of 2NP

^a Residence time 0.47 s. ^b Molar amount relative to propene.

the shorter (r = 18 mm, x = 14 mm) reactor filled with 0.5 kPa of SF₆ and 39.4 kPa of helium. The dependence of the decomposition of 2NP on time is shown in fig. 4, together with that of the reference reaction, decomposition of EA. The rate of both decompositions decreases upon addition of diluent gas (argon or helium). The greater decrease in rate observed with helium (in its presence EA does not decompose at all) is consistent with its higher thermal conductivity. Relative (mean) rate constants k_{2NP} : k_{EA} calculated for reactant + SF₆ (4.2) and reactant + SF₆ + Ar (2.8) systems allow one to estimate the mean effective temperature, $\langle T \rangle$; its value calculated for three different mechanistic paths to 2NP decomposition, namely, partly heterogeneous, molecular and homolytic bond-fission, are gathered in table 1. The Arrhenius

parameters of the first two reactions yield values of $\langle T \rangle$ for the system reactant + SF₆ which are lower than for the system reactant + SF₆ + argon. In contrast, and in accord with the calculated temperature distributions (fig. 3) and reaction rates (fig. 4) for the systems in question, the higher $\langle T \rangle$ value for the system without argon is obtained by considering Arrhenius parameters for the C—N bond-fission mechanism. It thus appears that from the two possible (and competing¹⁰) mechanisms of 2NP decomposition operating in the photosensitized experiments, *i.e.* the molecular and C—N bond-fission mechanisms, the latter is more important. In fact, the true temperatures in irradiated systems have to be higher than the effective temperature, and the occurrence of the C—N bond-fission mechanism in the photosensitized reaction is in agreement with the finding¹⁰ that C—N bond fission is favoured over molecular decomposition at temperatures > 700 K. Such an inference, taken together with the product analysis, supports a reaction scheme different from that valid for surface decomposition:

$$CH_3 \cdot CH(NO_2) \cdot CH_3 \rightarrow [CH_3 - CH - CH_3] \rightarrow CH_3 \cdot CH = CH_2 + HNO_2$$
$$--- + ---$$
$$NO_2$$

 $2HNO_2 \rightarrow H_2O + NO + NO_2$.

The surface reaction at temperatures < 700 K proceeds² via the molecular elimination of HONO, followed by a series of reactions between 2NP and the decomposition products of nitrous acid, yielding acetone, acetonitrile and formaldehyde. At higher temperatures the decomposition of HONO was implied⁶ to take place either by the bimolecular route or by a reaction with the wall. The product distribution of surface pyrolysis of 2NP at temperatures > 700 K is given in table 2. Noticeable yields of acetonitrile and acetone confirm the assumption of their surface formation during the photosensitized reaction. The most striking feature emerging from the comparison of the laser-powered homogeneous pyrolysis and the heterogeneous pulsed pyrolysis is the surface-facilitated formation of 2-nitropropene:

$$\begin{array}{c} CH_{3} \longrightarrow CH \longrightarrow CH_{3} \xrightarrow{surface} CH_{3} \longrightarrow CH_{2} \\ | \\ NO_{2} \end{array} \xrightarrow{O-H_{2}} CH_{3} \longrightarrow CH_{2} \\ | \\ NO_{2} \end{array}$$

This reaction obviously proceeds via dehydrogenation and should merit further attention since this non-polar type of reaction is favoured on a metallic surface over the competing modes¹⁰ (molecular and radical) of the elimination of HNO_2 . The yield of 2-nitropropene obtained in the pyrolysis at 820 K is 2.3 times higher than that of propene. The surface pyrolysis of 2NP may thus prove to be more efficient for preparative purposes than thermal methods in the production of propene.

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