IR-LASER-INDUCED SENSITIZED ORGANIC REACTIONS: AN EXAMPLE OF RATE CONTROL BY VIBRATIONAL ENERGY TRANSFER

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Summary

The CO_2-laser-induced decomposition of cyclohexene has been studied in the presence of SiF_4, SF_6 and C_6F_6 as sensitizers. The pressure range investigated is between 10 and 30 Torr at laser fluences between 0.20 and 1.20 J cm^{-2}. At the same time measurements of the IR multiphoton absorption of the three sensitizers were also performed.

The results have been analysed within the framework of a kinetic model based on the assumption that the rate is controlled by vibrational energy transfer from the multiphoton-excited sensitizer molecules to the reactant. Evidence is presented to show that these sensitized reactions proceed under non-equilibrium conditions.

1. Introduction

Photosensitization represents a method for carrying out a photochemical process when a molecule cannot be raised to the desired excited state by direct absorption of light.

Pulsed-IR-laser-induced processes are made possible, for molecules which do not appreciably absorb in the 9 - 11 μm region of the CO_2 laser, by the addition of a sensitizer (NH_3, SiF_4, SF_6 or C_6F_6) which, on the contrary, strongly absorbs in this region. The multiphoton excitation of the sensitizer is transferred via collisional processes to the given molecule which then reacts. A discussion of these sensitized processes can be found in refs. 1 - 5.

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The prevailing opinion is that the vibrational energy stored in the multiphoton-excited sensitizer molecules is readily thermalized by vibrational–rotational–translational (v–r–t) transfer processes: when the absorbed energy is effectively thermalized before the reactant is appreciably transformed the pulsed-laser-induced reaction can be regarded as a laser-powered homogeneous pyrolysis. These reactions are completed in times of the order of 10^{-5} s during the thermal spike which follows the laser pulse [2].

While laser-powered homogeneous pyrolysis has successfully been utilized to derive unknown kinetic parameters by a comparative rate method [2], it is the purpose of the present work to show that laser-induced sensitized reactions can also occur during the laser pulse (1 - 2 μs), i.e. before thermalization of the absorbed laser energy. This implies that reaction rates are controlled by the process of vibrational energy transfer from the multiphoton-excited molecules of the sensitizer to the reactant.

A distinction between a pyrolytic process in a thermalized system and a unimolecular reaction controlled by energy transfer in a typical non-equilibrium situation is important because the reaction rates should be related to the gas temperatures in the first case and to v–v energy transfer rates in the second case.

When effective thermalization of the absorbed laser energy occurs before appreciable decomposition of the reactant the following relationship holds for any pair of reactants i, j for a first-order dependence of the reaction rates on the reactant concentration and in the absence of a pressure fall-off of the unimolecular reactions:

$$-\ln(1 - y_i) = k_i \tau \tag{1a}$$

$$\frac{\ln(1 - y_i)}{\ln(1 - y_j)} = \frac{k_i}{k_j} = \frac{A_i}{A_j} \exp\left(\frac{E_j - E_i}{RT_c}\right) \tag{1b}$$
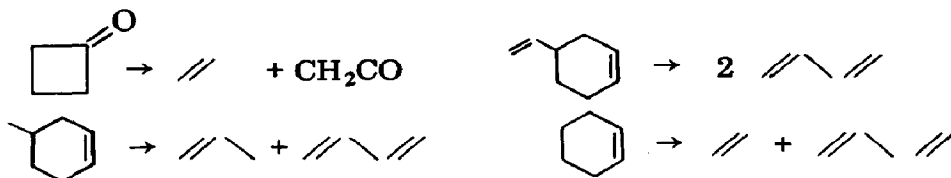
and

$$\tau = -\frac{\ln(1 - y_i)}{A_i} \exp\left(\frac{E_i}{RT_c}\right) \tag{1c}$$

where y_i, k_i, A_i and E_i are the fractional product yield per pulse, the first-order rate constant, the Arrhenius pre-exponential factor and the activation energy respectively for reactant i. τ is the reaction time and T_c is the so-called "chemical" temperature [3] of the gas. A chemical temperature calculated from the product yields in this manner should be independent of the reactant pair chosen and close to the temperature of the sensitizer–reactant gas mixture computed from the absorbed laser energy and the specific heat of the mixture on the assumption of adiabatic heating and of full thermalization [2, 3].

In ref. 6 the following sensitized reactions were investigated in the presence of excess SF_6 (5:1) in the pressure range 10 - 30 Torr at absorbed

laser energies of $250 \text{-} 450$ kJ mol^{-1} (P20 line of a pulsed 1.6 μs CO_2–TEA laser).

$$\square\hspace{-0.5em}=\!O \rightarrow //\ + CH_2CO \qquad\qquad \rightarrow 2\ //\diagdown//$$

$$\rightarrow //\diagdown + //\diagdown// \qquad\qquad \rightarrow //\ + //\diagdown//$$

The "chemical" temperatures, reaction times and pressure dependences of the k_i determined in ref. 6 were shown to be inconsistent with the behaviour expected for a thermalized system [6, 7].

The purpose of the present paper is to clarify these rather unexpected results. The decomposition of cyclohexene has therefore been investigated under conditions similar to those of ref. 6, but in the presence of different sensitizers, namely SiF_4, SF_6 and C_6F_6.

As a consequence of the different values of the specific heats of the three sensitizers, their adiabatic temperatures, at the *same* absorbed laser energy, are very different and one would therefore expect large differences in the rate constants for the three thermalized systems.

In fact, at an absorbed energy of 2.0×10^5 J mol^{-1}, the rate constants

$$k_i = 2 \times 10^{15} \exp\left(-\frac{33\,700}{T}\right)$$

for cyclohexene decomposition calculated according to ref. 8 should be in the ratio $1:(2 \times 10^{-2}):(4 \times 10^{-7})$ for SiF_4, SF_6 and C_6F_6 respectively. The corresponding ratios measured in the present work are $1:(1 \times 10^{-1}):(4.5 \times 10^{-2})$.

These results show that, under the present experimental conditions, the assumption of v–r–t equilibration before reaction is indeed untenable. The possibility should thus be explored that these sensitized reactions occur during the laser pulse and before the equilibration of the laser energy or, in other words, that the rate of the unimolecular decomposition is actually determined by the rate of the vibrational energy transfer from the multi-photon-excited molecules of the sensitizers to the reacting organic molecule. The present results and those obtained previously will therefore be analysed following the kinetic model proposed in ref. 7.

2. Experimental details and results

Vibrational excitation of the three sensitizers was carried out by means of a pulsed grating-tuned CO_2–TEA laser, for SF_6 using the P20 lines of the 001–100 band of CO_2 (944 cm^{-1}) and for SiF_4 and C_6H_6 using the P34 line of the 001–020 band of CO_2 (1033 cm^{-1}).

The laser gas mixture consisted of helium, CO_2 and N_2 in the ratio 3:1:1. The energy output of the laser through a metal slit was 0.1 J (pulse)$^{-1}$ with a duration of about 1.8 μs.

A combination of mirror, slit and lens optical elements was used to confine the laser beam to a cross section of approximately 0.1 cm^2. Attenuation with thin films of polyethylene provided a chemically useful range of fluences between 0.35 and 1.20 J cm^{-2}.

The irradiations of the gas mixtures took place in a cylindrical double-sided stainless-steel cell of variable length and internal diameter 3 cm, with antireflection coated ZnSe windows 3 mm thick sealed at the ends. Two side connections of internal diameter 1 mm led, through appropriate valves, to vacuum and/or gas handling equipment and a flame ionization detection gas chromatograph. The gas pressures were monitored by means of an MKS baratron gauge.

The mixtures of reactant and sensitizer contained 8% cyclohexene in SF_6 and 7% cyclohexene in both SiF_4 and C_6F_6. All samples were carefully degassed on a conventional vacuum line before use.

The gas chromatographic determination of the fractional conversion was obtained by using known amounts of ethylene as a reference gas.

While SF_6, SiF_4 and to a lesser extent C_6F_6 were found to be inert, cyclohexene exhibited extensive physisorption on the stainless steel surfaces. In order to avoid depletion of the reactant substrate in the reaction cell, the surfaces were completely saturated by allowing the gas mixture to flow slowly from a large reservoir through the cell into another evacuated reservoir, until the desired pressure was attained. This procedure ensured that the final gas composition in the reaction cell was the same as that prepared.

The multiphoton absorption of the laser energy by SF_6, SiF_4 and C_6F_6 was measured by means of a calibrated joulemeter. The experimentally determined dependence of the absorbed energy $E_A(t_p)$ per mole of sensitizer on the inlet fluence F^0 (J cm^{-2}) is plotted in Fig. 1(a) for SF_6, SiF_4 and C_6F_6 at the same pressure P = 30 Torr.

At the laser frequencies used in the experiments cyclohexene is virtually transparent. This was confirmed by the observed absence of reaction products when a sample of 2 Torr pure reactant was exposed to a laser fluence of up to 2 J cm^{-2}.

The experiments were carried out under optically thin conditions. The cell length was adjusted so that for each sensitizer and each pressure the absorbance did not exceed 20% (minimum cell length, 0.6 cm). The fractional product yields y_i per pulse become independent of cell length below about 20% absorbance. A correction to the beam diameter was applied in the case of SF_6 as a consequence of non-negligible self-focusing.

Figures 2(a) and 2(b) show the results obtained at different pressures for SiF_4 and C_6F_6 respectively. In these figures the logarithm of the average rate constant $\bar{k}_i$ multiplied by the laser pulse duration t_p, calculated according to eqn. (1a) from the measured fractional product yields y_i, has been plotted against the reciprocal of the energy $E_A(t_p)$ absorbed by one mole of sensitizer during the period t_p of the laser pulse.
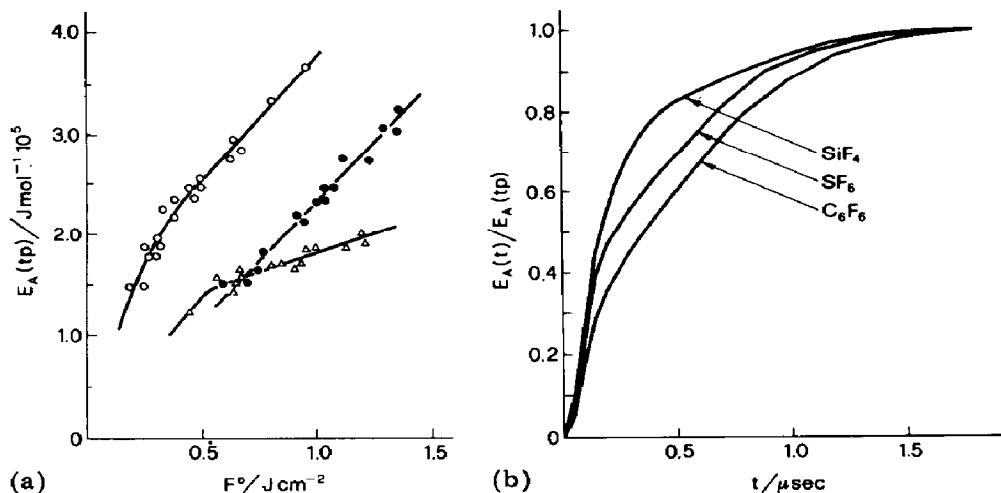
Fig. 1. (a) Plot of the total energy $E_A(t_p)$ absorbed during the laser pulse *vs.* the fluence F^0, measured at the entrance of the gas cell, for SiF_4 ($\triangle$), SF_6 ($\circ$) and C_6F_6 ($\bullet$) at 30 Torr. (b) Time evolution of the ratio $E_A(t)/E_A(t_p)$ between the total absorbed energy at time t and the total energy absorbed during the laser pulse: C_6F_6, $F^0 = 1.0$ J cm^{-2}; SF_6, $F^0 = 0.6$ J cm^{-2}; SiF_4, $F^0 = 1.0$ J cm^{-2}.
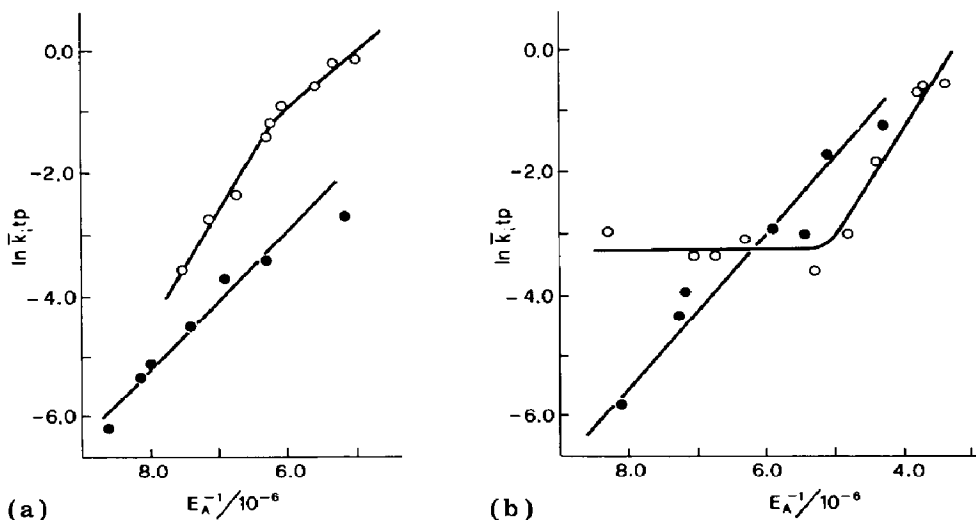

Fig. 2. (a) Semilogarithmic plots of $\bar{k}_i t_p$ *vs.* $E_A(t_p)^{-1}$ for cyclohexene in SiF_4 at total pressures of 20 ($\bullet$) and 30 ($\circ$) Torr. (b) Semilogarithmic plots of $\bar{k}_i t_p$ *vs.* $E_A(t_p)^{-1}$ for cyclohexene in C_6F_6 at total pressures of 10 ($\bullet$) and 30 ($\circ$) Torr.

Figure 3 shows the results for SF_6 at 10, 20 and 30 Torr. The thin line gives the least-squares fit through the experimental points at 20 and 30 Torr uncorrected for self-focusing. The corrected fit is given by the bold line. The lines through the points in Figs. 2(a), 2(b) and 3 have been calculated as specified in Section 3.
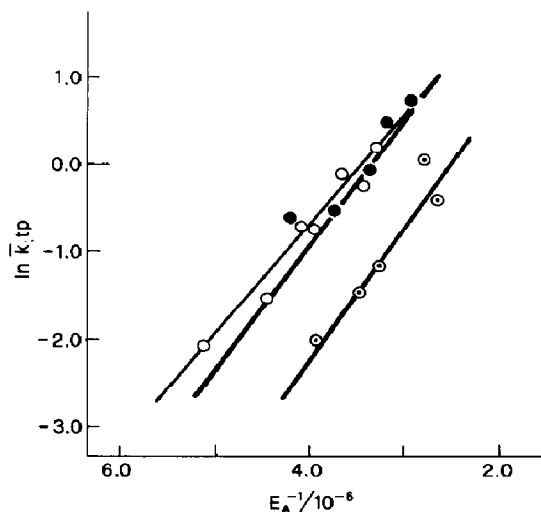
Fig. 3. Semilogarithmic plot of $\bar{k}_i t_p$ vs. $E_A(t_p)^{-1}$ for cyclohexene in SF_6 at total pressures of 10 (⊙), 20 (●) and 30 (○) Torr.

3. Discussion

3.1. Kinetic model

The model is based on the following considerations.

The total absorbed energy $E_A(t)$ (J mol^{-1}) per mole of sensitizers is a function of time determined by the laser pulse shape and by the characteristics of the absorber.

The laser pulse shape can be obtained from the oscilloscope trace of the laser intensity (in watts per reciprocal centimetre squared) during the pulse. From these intensity–time curves, the corresponding fluence–time functions can be derived by integration and, by taking into account the reported trend of $E_A(t_p)$ with the average fluence F^0 (Fig. 1(a)) the dependence of E_A on time can be calculated for the particular sensitizer and experimental conditions.

Typical $E_A(t)/E_A(t_p)$ versus t functions have been plotted in Fig. 1(b) for C_6F_6, SF_6 and SiF_4. Although the laser pulse shape is unchanged, these curves differ from one another and follow the different behaviour of $E_A(t_p)$ versus F^0 for the three sensitizers.

The vibrational energy $E_S(t)$ (J mol^{-1}) per mole of S is given by

$$E_S(t) = E_A(t) - 24.94\{T(t) - 298\}$$

where $T(t)$ (K) is the gas kinetic temperature at time t.

Sensitizer molecules with a vibrational energy $E_S(t)$ transfer to the reactant R, via v–v processes, an amount of energy α_v (J mol^{-1}) per mole of R per collision. It will be assumed that $\alpha_v = \alpha_v^0 E_S(t)$, i.e. $\alpha_v^0 = \alpha_v/E_S(t)$ is defined as the fraction of vibrational energy $E_S(t)$ per mole which is transferred per collision to R.

The general scheme for a unimolecular decomposition is [9]

$$R \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R^* \xrightarrow{k_a} R^+ \xrightarrow{k^+} \text{products}$$
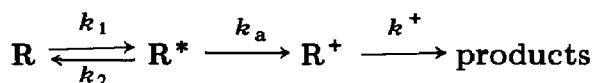
R^* denotes a reactant molecule with an internal energy higher than the threshold for dissociation (an energized molecule) and R^+ is the activated complex. The first-order rate constant for energization of R is k_1 (s^{-1}), and that for collisional deactivation of R^* is $k_2 = k_2{}^0 n$, (n, mol cm^{-3}) and k_a and k^+ refer to the processes $R^* \to R^+$ and $R^+ \to$ products respectively.

In the present model the energization of R is assumed to be dominated by the v–v energy transfer process from excited S molecules.

As a consequence of this transfer of energy, the vibrational energy $E_R(t)$ (J mol^{-1}) per mole of R will increase with time and according to RRKM theory [9] R will decompose to products at a rate corresponding to its vibrational energy.

If we assume that the vibrational energy $E_R(t)$ of the reactant is partitioned according to a Boltzmann distribution and is essentially unperturbed by the dissociation reaction, then we may employ the limiting high pressure rate constant for unimolecular thermal decompositions. Thus, for a given $E_R(t)$ the corresponding first-order rate constant $k_i(t)$ for decomposition may be written as

$$k_i(t) = A_i \exp\left[-\frac{E_i}{R T\{E_R(t)\}}\right] \tag{2}$$

where A_i and E_i are literature data referring to the high pressure limit of the relevant thermal unimolecular reaction and $T\{E_R(t)\}$ is the temperature corresponding to the vibrational energy $E_R(t)$ of the reactant. Values of $T\{E_R(t)\}$ can be calculated according to standard methods from the frequencies of the vibrational modes of the reactants under investigation [7, 10, 11].

From the above assumption it follows that the problem of calculating $k_i(t)$ during the laser pulse is reduced to the evaluation of $E_R(t)$.

The instantaneous energy balance for one mole of R is

$$\frac{dE_R(t)}{dt} = Z n x_S \alpha_v{}^0 E_S(t) - E_R(t)(k_i + k_2) \tag{3}$$

where Z is in centimetres cubed per mole per second and n is in moles per reciprocal centimetre cubed, and x_S is the mole fraction of S in the gas mixture.

The first term on the right-hand side of eqn. (3) gives the net input of vibrational energy from excited S per mole of R per second, whereas the second term represents the energy losses due to both reaction ($k_i E_R(t)$) and to collisional deactivation ($k_2 E_R(t)$).

It has to be pointed out, however, that eqn. (3) cannot be integrated analytically to yield $E_R(t)$, because of the exponential relationship between k_i and $E_R(t)$ (eqn. (2)) and because k_2 and its dependence on $E_R(t)$ are not known. Use has therefore been made of an empirical integral equation,

$$-\ln\left\{\frac{1-E_R(t)}{E_R^\infty}\right\} = Znx_S\alpha_v^0\frac{E_S(t_p)}{E_R^\infty}F(t) \tag{4}$$

which successfully fitted the experimental data. E_R^∞ and α_v^0 are obtained from the fitting procedure (see below, Section 3.2).

When $T(t) - 298 \approx 0$, the quantity $E_S(t_p)F(t)$ becomes approximately $E_A(t_p)F(t)$ and corresponds to the integral

$$\int_0^t E_A(t)\,\mathrm{d}t$$

$F(t)$ is therefore the integral up to time t of the relevant function of Fig. 1(b).

It is easily seen that eqn. (4) is derived from the differential equation

$$\frac{\mathrm{d}E_R(t)}{\mathrm{d}t} = Znx_S\alpha_v^{0\prime}E_S(t)\{E_R^\infty - E_R(t)\} \tag{4'}$$

Comparison of eqn. (4') with eqn. (3) yields

$$\alpha_v^{0\prime} = \frac{\alpha_v^0}{E_R^\infty}$$

$$k_i + k_2 = Znx_S\alpha_v^0\frac{E_S(t)}{E_R^\infty} \tag{4''}$$

Therefore the empirical differential equation (eqn. (4')) will be coincident with the exact differential equation (eqn. (3)) when eqn. (4") holds. The functions $E_R(t)/E_R^\infty$ calculated by means of eqn. (4) are shown in ref. 7 (Figs. 3(a) and 3(b)) together with the corresponding $k_i(t)$ functions.

Integration of these $k_i(t)$ functions up to time t_p yields the quantities $\bar{k}_i t_p$ which are related to the observed fractional product yields y_i by

$$\bar{k}_i t_p = -\ln(1 - y_i)$$

$\bar{k}_i$ is therefore the mean value of $k_i(t)$ during the laser pulse.

A comparison between the function $E_R\{t, k_2(t)\}$, calculated from eqn. (3) by performing a numerical integration using eqn. (2) and with $k_2(t)$ as a parameter, with the corresponding function $E_R(t)$, derived from the fitting of eqn. (4), allows the function $k_2(t)$ which satisfies eqn. (4") to be determined.

When multiphoton absorption takes place at sufficiently high pressures (above a few torrs), de-excitation of the sensitizer by v–r–t processes may become important, so that a fraction of the stored vibrational energy is lost

to the heat bath, whose temperature $T(t)$ will progressively increase [12]. In this case $T(t) - 298 > 0$ and $E_A(t) > E_S(t)$.

The total energy balance is now

$$\frac{dE_A(t)}{dt} = \frac{dE_S(t)}{dt} + \frac{1}{x_S}\frac{dE_{BS}(t)}{dt} + \frac{x_R}{x_S}\frac{dE_R(t)}{dt} \tag{5}$$

$E_{BS}(t)$ is the energy transferred by S to the bath. In the presence of collisional deactivation $E_S(t)$ is characterized by a pressure-dependent maximum occurring at a pressure-dependent time $t_{max} \leqslant t_p$ [7, 12]. At $t = t_{max}$, $dE_S(t)/dt = 0$ and

$$\left\{\frac{dE_A(t)}{dt}\right\}_{t_{max}} = \bar{Z}n\alpha_T + Zx_R n\alpha_v{}^0 E_S(t_{max})\left\{1 - \frac{E_R(t_{max})}{E_R{}^\infty}\right\} \tag{6}$$

$\bar{Z}n\alpha_T = (1/x_S)\,dE_{BS}(t)/dt$ gives the net rate of v–r–t energy transfer from excited S to the bath and is one term responsible for the temperature increase of the gas mixture. $\bar{Z}$ is given by

$$\bar{Z} = x_S Z_{S-S} + x_R Z_{S-R}$$

A second term responsible for the temperature increase of the gas mixture originates from collisional deactivation of excited R molecules and according to eqn. (3) can be expressed by

$$\frac{dE_{BR}}{dt} = x_R E_R(t)k_2(t) \tag{7}$$

where E_{BR} is the energy transferred by R to the bath.

The consequences of collisional deactivation on $E_R(t)/E_R{}^\infty$ and on $k_i(t)$ are illustrated by the broken lines in Figs. 3(a) and 3(b) of ref. 7 and by Fig. 5 of ref. 12.

The largest contribution to the reactant decomposition is now restricted to times in the vicinity of t_{max}.

3.2. Analysis of experimental data

The fitting of the data reported in Figs. 2 and 3 to eqn. (4) is performed as follows.

Starting from the lowest pressure investigated, negligible collisional deactivation is assumed, i.e. $F(t) = F(t_p)$ with $F(t_p)$ depending on the various sensitizers, as can be appreciated from Fig. 1(b).

From

$$\ln\{-\ln(1 - y_i)\} = \ln \bar{k}_i t_p = \ln A_i t_p - \frac{E_i}{RT(\bar{E}_R)}$$

the $\bar{E}_R$ corresponding to $\bar{k}_i$ at different values of $E_A(t_p)$ are obtained.

The experimental data are then fitted to eqn. (4) by determining $E_R{}^\infty$ by trial and error, and thus a value of $Z\alpha_v{}^0$ is obtained which is by definition independent of pressure.

TABLE 1

Values of α_v^0, E_R^∞ and t_{eff} for the sensitizers SF_6, C_6F_6 and SiF_4

P (Torr)	$\alpha_v^0 \times 10^{-2}$	E_R^∞ (kJ mol^{-1})	t_{eff} (μs)
SF_6			
30	1.12	330	0.84
20	1.12	320	1.14
10	1.12	310	1.8
C_6F_6			
30	1.82	350	0.60, 0.75
10	1.82	320	1.36
SiF_4			
30	0.54	320	1.67, 1.50
20	0.54	310	1.8

It is found that fitting at higher pressures is still possible with the same α_v^0 provided that the integration of the curves of Fig. 1(b) is carried out up to a time $t = t_{eff}$ shorter than the pulse duration (*i.e.* $t_{eff} < t_p$, with t_{eff} depending on the pressure and the sensitizer) or in other words that a value $F(t) = F(t_{eff}) < F(t_p)$ is used in eqn. (4).

Values of t_{eff} for different sensitizers and pressures are listed in Table 1.

The lines through the points of Figs. 2 and 3 are the results of this fitting procedure and they essentially coincide with the corresponding least-squares fits. The scatter of the points is rather large in all cases and should be related to fluctuations in both the energy and the shape of the laser pulses.

3.2.1. Evaluation of energy transfer quantities

3.2.1.1. α_v^0. The fitting procedure yields $Z\alpha_v^0$. The values of α_v^0 reported in Table 1 were derived after evaluation of Z for the three sensitizers using the following collision diameters: SiF_4, 6.3×10^{-8} cm [13]; SF_6, 5.5×10^{-8} cm [13]; C_6F_6, 7.0×10^{-8} cm [14]; cyclohexene, 6.1×10^{-8} cm [15].

The rate of v–v energy transfer from sensitizer S per mole of reactant R is $Z\alpha_v^0 E_S n x_S$ (J mol^{-1} s^{-1}) (eqn. (3)), with $Z\alpha_v^0$ specific to each S–R pair.

The values of $Z\alpha_v^0$ determined in the present work together with those for cyclobutene, cyclohexene, 4-methylcyclohexene and 4-vinylcyclohexene in excess SF_6, derived in ref. 7, when analysed in terms of the product $S_S S_R$ of the numbers S_S and S_R of internal degrees of freedom ($3N - 6$) of the sensitizer and the reactant respectively, show a linear dependence of the type

$$Z\alpha_v^0 = 3.8 \times 10^9 S_S S_R$$

The quantities $\alpha_v = \alpha_v^0 E_S$ derived in the present work give the net amount of energy transferred per collision from the vibrational states of the sensitizer, which are immersed in the quasi-continuum of the rovibrational manifold, to the very dense manifolds of the reactants investigated. They are therefore essentially different from those determined for v–v transfer pro-

cesses between discrete vibrational levels of collision partners. In fact, literature values for near-resonant v–v processes are of the order of $10^{-2}h\nu$, while the present values are in the range 1 - 6 kJ mol^{-1} or $(0.9 - 5) \times 10^{-1}h\nu$, i.e. are larger by approximately one order of magnitude and are apparently proportional to the product of the numbers of internal degrees of freedom of the two collision partners [16].

3.2.1.2. $k_2(t)$ and $\alpha_T{}^R$. Once $Z\alpha_v{}^0$ and $E_R{}^\infty$ have been determined, the $E_R(t)$ can be evaluated by means of eqn. (4). These functions can be compared, as specified in Section 3.1, with the corresponding $E_R(t, k_2(t))$ derived by numerical integration of eqn. (3). This allows the rate constant $k_2(t)$ for the collisional deactivation of R to be determined. The values of $k_2(t)$ have been plotted against $E_R(t)$ in Fig. 4(a) for typical conditions. $k_2(t)$ increases with $E_R(t)$ and tends towards saturation. It depends on pressure (as expected) and sensitizer.

The average energy transferred per collision from R (internal energy, $E_R(t_{eff})$) to the bath is $\alpha_T{}^R$ and relates to $k_2(t_{eff})$ according to

$$E_R(t_{eff})k_2(t_{eff}) = Z_{S-ch}n\alpha_T{}^R$$

(ch, cyclohexene) which is one of the two terms responsible for the temperature increase of the gas mixture (see Section 3.1).
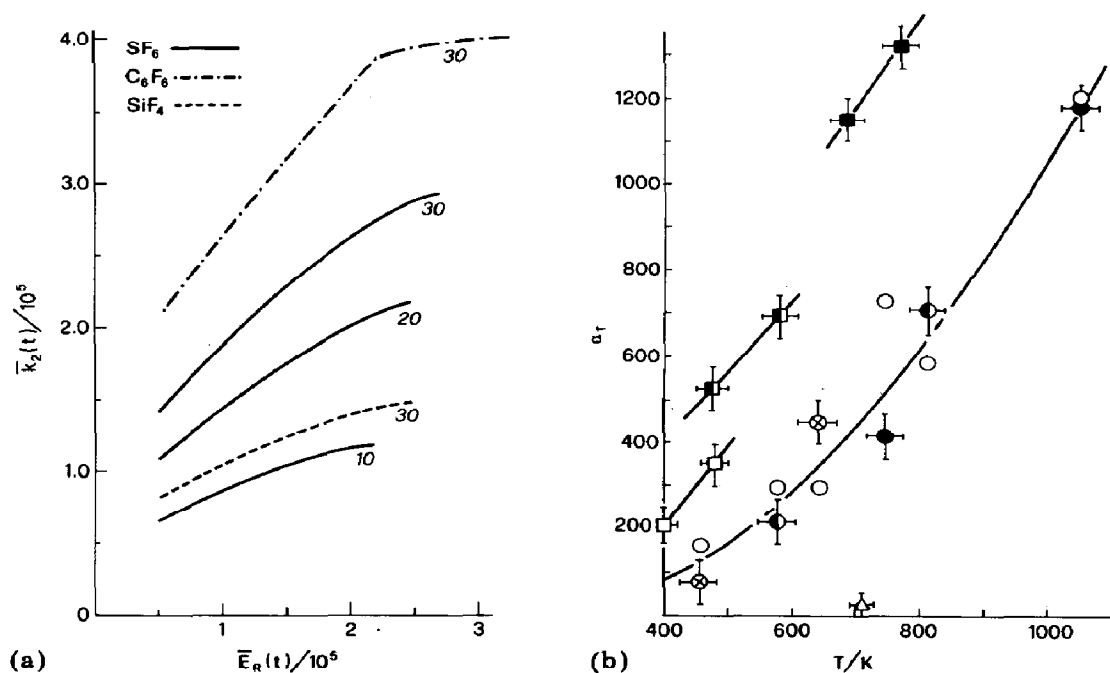

Fig. 4. (a) $\bar{k}_2(t)$ as a function of $\bar{E}_R(t)$ for the three sensitizers at different pressures (indicated on curves). $E_A(t_p)/10^5$ (J mol^{-1}) is 3.33 for SF$_6$, 3.00 for C$_6$F$_6$ and 2.00 for SiF$_4$. (b) Plots of the v–t transfer coefficient α_T (J mol^{-1}) as a function of gas temperature T. SF$_6$: ●, $E_A(t_p)/10^5$ = 3.33 J mol^{-1}; ◐, $E_A(t_p)/10^5$ = 2.50 J mol^{-1}; ⊛, $E_A(t_p)/10^5$ = 2.00 J mol^{-1}; ○, from ref. 17. C$_6$F$_6$: ■, $E_A(t_p)/10^5$ = 3.00 J mol^{-1}; ◫, $E_A(t_p)/10^5$ = 2.00 J mol^{-1}; □, $E_A(t_p)/10^5$ = 1.49 J mol^{-1}. SiF$_4$: △, $E_A(t_p)/10^5$ = 2.00 J mol^{-1}.

3.2.1.3. α_T. When $t_{eff} < t_p$, the quantity α_T, defined by eqns. (5) and (6), can be determined together with the bath temperature at $t = t_{eff}$, as specified in Appendix A. α_T is the average energy transferred per collision by the sensitizer (internal energy, $E_S(t_{eff})$) to the bath. $\bar{Z}n\alpha_T$ is the other term responsible for heating the gas. Values of α_T for the three sensitizers have been plotted in Fig. 4(b) as a function of the computed gas temperature at $t = t_{eff}$. The symbols refer to different values of $E_A(t_p)$; different points with the same symbol correspond to different pressures. The open circles (for SF_6) have been derived from ref. 17 as specified in Appendix A.

The agreement with ref. 17 can be considered fair within the uncertainties involved in this indirect derivation of α_T and T.

In Table 2 values of α_v, α_T and α_T^R for typical conditions have been collected for purpose of comparison.

The average vibrational energy α_v transferred per collision by the sensitizer to the vibrational manifold of the reactant is larger by a factor of at least 4.5 with respect to the corresponding vibrational energy α_T given up by S to the translational and rotational degrees of freedom of the molecules of the gas mixture.

However, the average vibrational energy α_T^R lost by the reactant to the gas bath is larger and of the order of $0.7\alpha_v$. This explains the large contribution to the heating of the gas from excited R, in spite of the small molar fraction of reactant in the mixtures.

Typical percentage contributions to gas heating by collisional deactivation of R, expressed as $(E_{BR}/E_B) \times 100$ (see Appendix A) are: SF_6, 26% at 30 Torr, 50% at 20 Torr and 90% at 10 Torr; C_6F_6, 23% at 30 Torr and 45% at 10 Torr; SiF_4, 90% at 30 Torr and 100% at 20 Torr.

3.2.2. Pressure dependence of $\bar{k}_i t_p$

Special attention should be paid to the different pressure dependences observed with the three sensitizers.

The largest dependence of $\bar{k}_i t_p$ on pressure is observed with SiF_4 (Fig. 2(a)), where a change in pressure from 30 to 20 Torr at $E_A(t_p) > 6.5 \times 10^{-6}$ J mol^{-1} lowers $\bar{k}_i t_p$ by a factor of 6. No decomposition has been observed up to 15 Torr. C_6F_6 (Fig. 2(b)) shows the opposite trend with a negative pres-

TABLE 2

Values of α_v, α_T and α_T^R (kJ mol^{-1}) (total pressure, 30 Torr)

Sensitizer	$E_A(t_p)$	α_v	α_T	α_T^R
SF_6	333	5.7	1.20	4.3
SF_6	200	2.7	0.45	1.8
C_6F_6	200	3.2	0.70	2.1
SiF_4	200	1.6	(0.02)	1.3

sure dependence between 10 and 30 Torr at $E_A(t_p)^{-1} > 6.5 \times 10^{-6}$ J mol^{-1}, and large and positive below this value. SF$_6$ (Fig. 3) exhibits an intermediate behaviour with no pressure dependence between 30 and 20 Torr and a large (above 1) dependence below 20 Torr.

These results are understandable if one assumes that thermalization occurs before reaction. In fact, for a thermal unimolecular reaction in the high pressure limit, $\bar{k}_i t_p$ is independent of pressure; in the unimolecular fall-off region, rate constants do become pressure dependent, but the order with respect to pressure does not exceed one.

As already mentioned, fitting of the data to eqn. (4) is first performed at the lowest pressures where it is assumed that collisional deactivation is small, i.e. $t_{eff} \approx t_p$.

Extension of the procedure to higher pressures, when $\alpha_v{}^0$ is independent of pressure, requires integration up to $t_{eff} \leqslant t_p$. When t_{eff} and t_p are not very different the full large pressure dependence predicted by eqn. (4) should be observed. This is clearly the case for SiF$_4$ (Table 1 and Fig. 2(a)).

When $t_{eff} < t_p$ the pressure dependence of $\bar{k}_i t_p$ is decreased because $k_i(t)$ is integrated over a shorter time interval. This can explain the pressure behaviour of SF$_6$ (Table 1 and Fig. 3). C$_6$F$_6$ is characterized by the highest values of α_T and shows an inverted pressure dependence above $E_A(t_p) \approx 1.5 \times 10^5$ J mol^{-1}, because t_{eff} at 30 Torr is now as low as 0.6 μs (Table 1 and Fig. 2(b)). Below this value of $E_A(t_p)$, t_{eff} rises to 0.75 μs and the $\ln \bar{k}_i t_p$ versus E_A^{-1} curve bends and remains essentially constant. This behaviour of t_{eff} is related to the increase in α_T with $E_A(t_p)$ shown in Fig. 4(b) for C$_6$F$_6$. The bending of the SiF$_4$ curve at 30 Torr (Fig. 2(a)) can be ascribed to similar causes. Notice that no bending is observed in the plots of Figs. 2 and 3 at the lowest pressures where $t_{eff} \approx t_p$.

This complex dependence of rate constants on pressure and $E_A(t_p)$, which is specific for each sensitizer, can therefore be ascribed in the present treatment to the specific dependences of the α_T on temperature and E_S and to the different values of $\{dE_A(t)/dt\}_t$ which together determine the values of $t_{max} \approx t_{eff}$ through eqn. (6).

At the lowest pressures, where deactivation of S by v–r–t transfer is smaller, the reaction time τ can actually be larger than t_p, because it takes time to stop the reaction. However, this difference between τ and t_p cannot be derived from present data since, referring to eqn. (4), $F(\tau) = F(t_p)$, and $\alpha_v{}^0$ and $E_R{}^\infty$ become rather insensitive to τ for $\tau > t_p$: e.g. for $\tau = 2t_p$ we obtain the same fit to the data with values of $\alpha_v{}^0$ and $E_R{}^\infty$ which differ by less than 5% from those reported in Table 1 and are therefore within the uncertainties involved in this type of fit.

4. Conclusions

Present and previous [6, 7] results for the pulsed IR-laser-induced sensitized decomposition of cyclocompounds do not conform to a model

of rapid thermalization of the laser energy absorbed by the sensitizers but can instead be rationalized on the assumption that the rate of the unimolecular decomposition of the cyclocompounds is controlled by the rate of vibrational energy transfer from the sensitizers to the reactants.

The data reported in Table 2 are important because they indicate that transfer of vibrational energy between excited sensitizer and reactant is sufficient to cause appreciable decomposition during the laser pulse, while the gas temperature remains sufficiently low to prevent any thermal contribution to the reaction. The conditions for a thermal regime of the reaction are the opposite. In this case, there should be no appreciable decomposition of the reactants before extensive thermalization of the absorbed laser energy has occurred. The system should furthermore be allowed to remain at a sufficiently high temperature for a sufficiently long time ($T = 800 - 1300$ K and $t \approx 10$ μs for the reactions studied in refs. 2 and 3).

These conditions can be attained but require a proper regulation of the term $\bar{Z}n\alpha_T$, which contributes to the rate of v–r–t transfer from the absorber to the gas bath and limits $E_S(t)$ and $E_R(t)$ to $E_S(t_{eff})$ and $E_R(t_{eff})$ respectively. This means that the pressure, composition and specific heat of the gas mixture must be properly selected. α_v/α_T should be as close as possible to unity as should the ratio between the laser-irradiated volume and the cell volume to preserve sufficiently high temperatures during expansion of the laser-heated volume. The shock waves arising from this expansion should also be properly considered.

The above conditions have been satisfied in the experiments described in refs. 2 and 3 as confirmed by the validity of eqn. (1) in these systems. The present results as well as those of refs. 6 and 7 provide, on the contrary, examples of sensitized reactions under non-equilibrium conditions.

Acknowledgments

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Appendix A

In order to evaluate α_T use can be made of eqn. (6) after setting t_{eff} equal to t_{max}. The various terms in this equation are determined as follows. $\{dE_A(t)/dt\}_{t_{eff}}$ is the derivative at $t = t_{eff}$ of the $E_A(t)$ functions evaluated for a specific sensitizer at the pressure and $E_A(t_p)$ of the experiment. Three such functions are those reported in Fig. 1(b). $E_S(t_{eff})$ is derived from $E_A(t_{eff})$ as indicated in Section 3.1. $E_R(t_{eff})$ can be calculated from eqn. (4) with known $Z\alpha_v^0$ and E_R^∞. In order to compare values of α_T with data from ref. 17 the following procedure has been adopted.

The theoretical model developed in ref. 17 requires that the probability $P_{i-1,i}$ that a collision will change the vibrational quantum number from i to $i - 1$ is proportional to the quantum number i.

$$P_{i-1,i} = iP_{0-1}$$

P_{0-1} is the probability for the 1—0 transition and is related to the experimental relaxation time τ_{v-t} for v—t transfer in SF_6 determined in ref. A1 as a function of temperature. One has

$$Z_{SF_6-SF_6}n\alpha_T = \frac{E_S}{\tau_{v-t}}$$

with $ih\nu = E_S$ and $h\nu = 11.3$ kJ mol^{-1}. This gives

$$\alpha_T = 5.8 \times 10^{-3}E_S T^{1/2} \exp\left(-\frac{38}{T^{1/3}}\right)$$

The temperature of the gas mixture at $t = t_{eff}$ is calculated as follows. The total energy E_{BS} transferred per mole of bath gas from S in a time $t = t_{eff}$ can be obtained from

$$E_{BS} = \bar{Z} x_S n \alpha_T{}^0 E_A(t_D) F(t_{eff}) \tag{A1}$$

derived from

$$\frac{dE_{BS}(t)}{dt} = \bar{Z} x_S n \alpha_T$$

with

$$\alpha_T = \alpha_T{}^0 E_A(t)$$

and

$$E_A(t_D) F(t_{eff}) = \int_0^{t_{eff}} E_A(t) \, dt$$

The total energy E_{BR} transferred per mole of bath gas from excited R in a time $t = t_{eff}$ is given by

$$E_{BR} = x_R \int_0^{t_{eff}} E_R(t) k_2(t) \, dt \tag{A2}$$

and can be evaluated by performing a numerical integration of eqn. (7), utilizing the $k_2(t)/E_R(t)$ from Fig. 4(a).

The total energy lost to the bath is therefore given by

$$E_B = E_{BS} + E_{BR}$$

The functions E_B/T for the various sensitizer–reactant mixtures can be calculated from thermodynamic data [7, 10], and the temperatures of the gas mixtures are thus easily obtainable. α_T and T should be calculated together by means of an iteration procedure because the terms in eqn. (6) are temperature dependent.

Reference for Appendix A

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