

Generation of Ketene with High Quantum Yield by a KrF Laser

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Acetone was photolyzed around 770 K by pulsed laser irradiation at 248 nm. The methyl radicals, generated in the primary step, trigger a chain reaction, producing ketene (CH_2CO) and methane. Long chains (high quantum yields) result from low radical concentrations. Using a collimated laser beam of low intensity, quantum yields up to 300 have been demonstrated. Approximate rate constants have been derived and used for extrapolation to higher temperatures and different densities. Compared to the thermal process, the photochemical formation of ketene is faster. Therefore its thermal decomposition can be avoided to some extent. But the improvement is probably too small to be of technical interest. We also found indications that the thermal decomposition of acetone above about 500 to 600 K yields three fragments in a single step.

Photochemical applications of lasers are usually based on their sharp wavelength, their high intensity and sometimes their short pulse lengths. Spatial collimation is used for photochemical etching and deposition on surfaces (writing). A very different application of spatial coherence has been found by Wolfrum and co-workers.¹ They synthesized vinyl chloride from 1,2-dichloroethane by a laser induced radical chain reaction. As in very many such reactions, the chain propagation is of first order, whereas the termination is of second order in the radical concentration. The chain length and the quantum yield are therefore the larger, the smaller the radical concentration, i.e., the smaller the radiation density and the larger the penetration depth. To attain the latter, a sharp wavelength in the wing of the absorption band is advantageous.

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However small radical concentrations also reduce the chain propagation rate and therefore the conversion per time and volume unit (thru-put). Therefore a compromise has to be found between high quantum yield and high thru-put. Depending on the kinetic constants of the case studied, such a compromise may be either easy to find, admitting any intensity, or it may require an intensity within narrow limits (e.g., within a factor of 3 to 5), or it may be impossible. In the intermediate case the laser is profitable: Nearly constant intensity over a large penetration depth means spatial collimation.

We investigated if this intermediate case applies to the generation of ketene from acetone:



This is a chain reaction initiated by CH_3 radicals (see below). Usually it is carried out thermally at a temperature around 1000 K, where acetone begins to decompose to CO and two methyl radicals:



This initiation reaction is the slowest step in the reaction sequence. If it is replaced by a photochemical generation of CH_3 , the temperature could be lowered. This is desirable, because ketene begins to decompose already above 700 K. So we looked for conditions where the ketene decomposition is still negligible, where the quantum yield is high and where the thru-put is not too small. To find such a compromise, we irradiated acetone at 768, 778 and 788 K by varying the energies of a KrF laser-pulse and determined six of the final products by gas-chromatography. These yields were modelled by rate equations to find out rate constants. The latter were then used to predict the best conditions of initial radical concentration (radiation density), pressure and temperature.

The KrF laser was selected because its wavelength (248 nm) is in the short wavelength wing of acetone and is only weakly absorbed. Ketene absorbs even more weakly because its spectrum lies at longer wavelengths than acetone (see section "Results").

The use of a pulsed laser for a low intensity application may appear disadvantageous at first sight. However with appropriate intensities, the reactions become slower than the repetition rates. Then the kinetics only depends on the average intensity.

The high temperature photochemistry of acetone has been investigated before by Brinton.² The photochemical and thermochemical decompositions of acetone and of ketene are reviewed in the book of Bamford and Tipper.³ The kinetics of the ketene pyrolysis is described by Guenther and Walters.⁴

EXPERIMENTAL

A commercial multigas excimer laser (Lumonics TE 262) was used. When operated as a KrF laser, the pulse width is about 22 ns. In order not to hit the cell wall the beam was limited by an iris to a diameter of 1.7 cm which was placed 30 cm in front of the entrance window of the cell. Intensity variation was obtained by putting infrared quartz plates in the laser beam as attenuators before the iris. Energies were measured by calibrated pyroelectric joulemeters (Gen Tec ED 200 for high intensity and Laser Precision RjP 735 for low intensity).

An all-quartz cell 114 mm long and 25 mm in inner diameter with 50 cm³ of total volume was used. A piezoresistive pressure gauge was mounted near the valve in the side arm of the cell, which reads the pressure of the reactions gas in the cell at high temperature. The valve and the pressure gauge were near room temperature. The fully heated volume of the cell was 56 cm³.

A copper cylinder, 32 cm long and 3.1 cm of inner diameter with 7 mm thick wall, was placed in a tube furnace with *UV* quartz windows. The copper tube and the windows reduced the temperature variation over the length of the oven to less than 1 K and probably to less than 0.1 K over the length of the cell. A temperature control unit with precision ± 0.5 K was used for the furnace. When the oven and cell reached the desired temperature, acetone vapor was filled into the cell. One minute later the cell was irradiated by a KrF laser with 2 pulses per second. After irradiation the cell was taken out of the oven and quenched with cold water. Then the sample was analyzed. The acetone (Merck) had spectroscopic grade.

A gas-chromatograph (Carlo Erba) was used for the analysis of the products. The column package was Chromosorb 101. The analysis of the products was carried out with the temperature rising linearly from 338 to 488 K.

RESULTS

Figure 1 shows the absorption spectra of acetone and ketene. At 248 nm the absorption cross-section σ of acetone is $2.4 \cdot 10^{-20} \text{ cm}^2$ (base e) at room temperature. At higher temperature it drops, since the spectrum not only broadens, but also moves to longer wavelengths. From the transmission of the laser through the 11.4 cm cell at 788 K we found $\sigma = 2.5 \cdot 10^{-20} \text{ cm}^2$. From the quantity of formed products (especially of ethane at high energy densities) the number of initial methyl radicals can be derived (see section "Kinetics"). Since it is established that two methyl radicals are formed per absorbed photon, σ can also be deduced in this way. We found $\sigma = 1.3 \cdot 10^{-20} \text{ cm}^2$. The correct cross-section is probably between these two values.

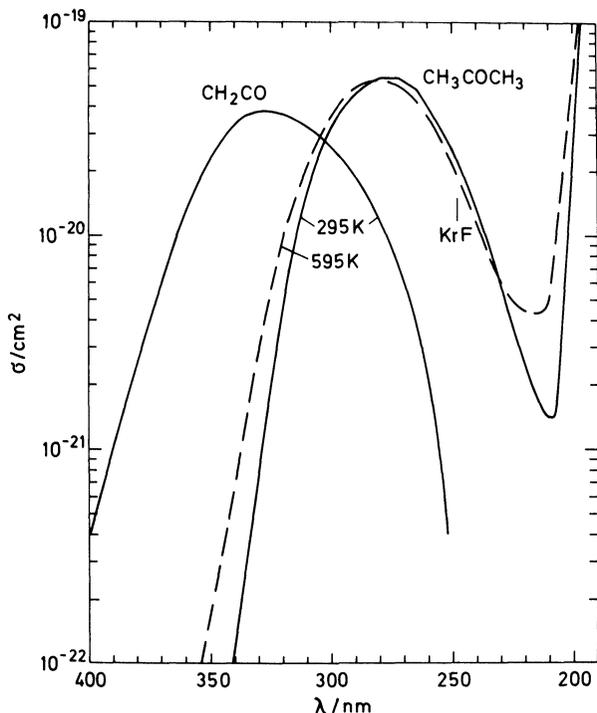


FIGURE 1 UV absorption spectra of acetone and ketene. The latter is taken from Ref. 9. The vibrational structure on its long-wavelength wing has been smoothed; its short-wavelength wing is taken from the liquid phase spectrum at 195 K.⁹

Figure 2 shows the measured quantities of products. They have been converted to concentrations, assuming the reactions take place only in the irradiated volume (21 cm^3 as compared to 59 cm^3 cell volume). From the data the dark reaction, measured under the same conditions, was subtracted. Since however the yields of dark and photochemical reactions are not additive, the uncorrected data are also given (broken lines) where the deviation was distinguishable.

All products were identified by their gas-chromatographic retention times only, comparing them with authentic samples. We did not try to detect CO , since we used a flame ionization detector. The yield of hexane-2,5-dione (Ac_2), the dimer of the acetyl radical, was apparently too small to be detected. The small yield was confirmed by the kinetic calculations. However the reason of this failure may also be technical. We did not find a signal from an authentic sample (vapor pressure 2 mbar) within 50 min under our gas chromatographic

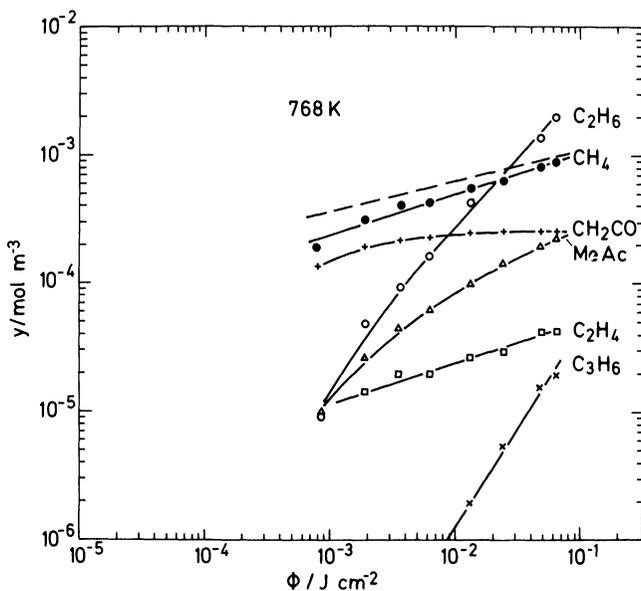


FIGURE 2 Product yields per pulse, y , (product quantities divided by the irradiated volume) as function of incident energy density per pulse, ϕ , for three different temperatures. Acetone density 2.77 mol/m^3 . (At room temperature $1 \text{ mol/m}^3 = 25.0 \text{ mbar}$). Solid lines and data points: yields after subtraction of the dark reaction. Yields including the dark reaction are given by the broken lines, where they differ noticeably.

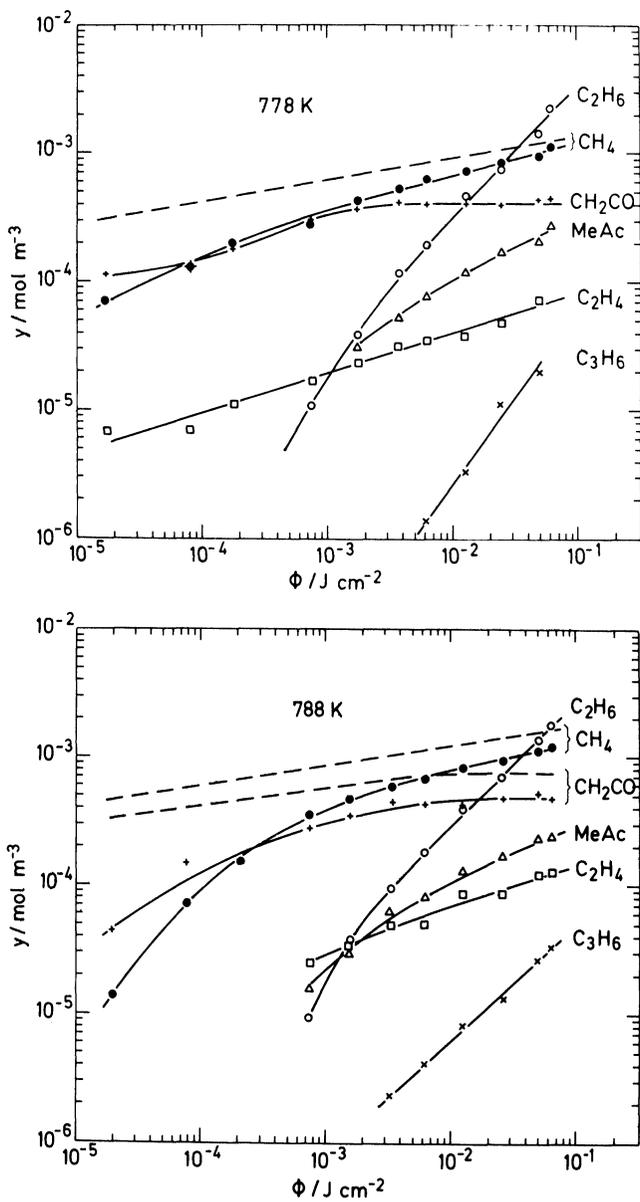
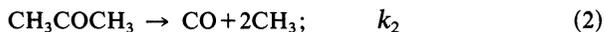


FIGURE 2 (cont.)

conditions. We did not find either allene, a decomposition product of ketene, and methyl vinyl ketone, a decomposition product of unclear origin. All three products have been found by Brinton.² However in addition to the ethene (probably a photolysis product of ketene) found by Brinton we also detected propene. Its retention time agreed with an authentic sample; it was however different from acetylene, cyclopropane, allene and diketene.

KINETIC MODEL

The kinetic description starts from the reaction scheme depicted in Figure 3. For the thermal initiation two possibilities are discussed



the latter with subsequent dissociation of acetyl:

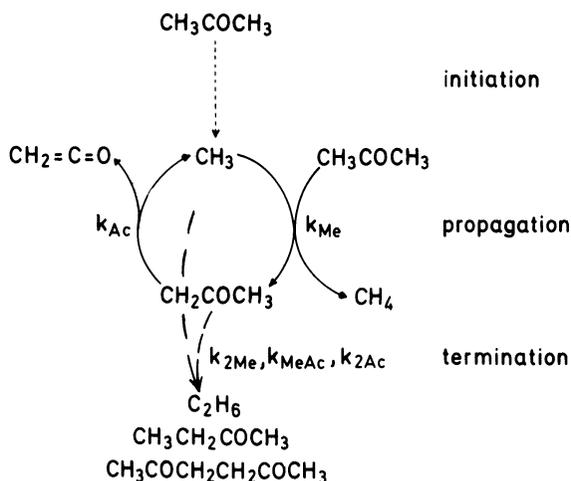


FIGURE 3 Reaction scheme. The subscripts of the rate constants refer to the educts of the reactions; Me = methyl, Ac = acetylonyl.

For photochemical initiation, $k_i = \sigma I / hf$ can be taken as rate constant, where I is the intensity of irradiation (W/cm^2) and hf is the photon energy ($8.0 \cdot 10^{-19} \text{ J}/\text{photon}$). For pulsed irradiation, as in our case, the calculation starts with an initial concentration Me_0 of methyl radicals:

$$\text{Me}_0 = \text{AcH} \cdot 2\sigma\phi / hf \quad (4)$$

where ϕ is the energy density (J/cm^2) and AcH is the acetone density. Thus we tried to simulate the results of Figure 2 by numerical integration of the rate equations corresponding to the reaction scheme of Figure 3, varying the rate constants and neglecting the side products C_2H_4 and C_3H_6 .

This attempt failed however, because the experimental data did not accurately comply with two balance equations required by the stoichiometry (e.g., by the balance of methyl and acetyl radicals) of Figure 3. These equations can be written:

$$\text{Me}_0 = \text{MeH} + \text{MeAc} + 2\text{Me}_2 - \text{Ket} \quad (5)$$

$$\text{Me}_0 = 2\text{Ac}_2 + 2\text{MeAc} + 2\text{Me}_2 \quad (6)$$

(Me = methyl, Ac = acetyl, Ket = ketene; Me_0 = initial methyl concentration, the other symbols denote final concentrations).

Obviously additional reactions (e.g., a loss of ketene) play a role. One of them is:



which is probably photochemical. So we added twice the C_2H_4 concentration to Ket . But there must be one more loss of ketene, maybe at the wall: otherwise in the dark reaction the methane and ketene concentrations should be equal. Another problem arises from the fact that we irradiated only 40% of the cell volume. However especially the propagation reactions also occur—after some diffusion—outside of the irradiated volume. This effect has been pointed out in Ref. 5. It tends to dilute the radical concentrations on the average, thus partially suppressing the termination by radical combination. If the reaction would have been confined to the irradiated volume, the relative concentrations Me_2 , MeAc and Ac_2 would have been larger than experimentally found.

Therefore in order to find out rate constants for the reaction scheme of Figure 3, we modified the concentrations found experimentally. These modifications are shown in Table 1. They were chosen in such a way as to minimize over a large range of Me_0 the difference of the two Me_0 calculated according to (5) and (6). That is, we tried to fulfil (8):

$$MeH - Ket = MeAc + 2Ac_2 \quad (8)$$

The correction for Me_2 was required to restore the proportionality between Me_0 and the laser energy. Only the correction of MeAc is large (30%), It probably reflects the effect of the non-confined irradiated volume, as does also the smaller correction of Me_2 . But all of these modifications are in our opinion small enough to still yield meaningful rate constants. Furthermore we confined the fit to the range of energy densities (100 to 10 mJ/cm²) where the dark reaction is negligible.

The rate constants thus found are shown in Table 2, together with previously reported figures. We found that variation of the methyl dimerization rate did not improve the fit. So for most calculations we took the reported value independent of temperature. On the other hand a substantial improvement was attained by variation of k_{Me} up to a value which is nearly twice as large as the highest value reported previously. The ratio $k_{MeAc}/(k_{2Me} \cdot k_{2Ac})^{1/2} \cong 2$, postulated by collision theory, was taken as criterion to select between fits of similar quality.

TABLE 1

Concentrations used for the computer fit and correction factors, c/c_{exp} , employed to the measured concentrations in order to fulfil Eq. 8. Me_0 = initial CH_3 concentrations; the other concentrations after a reaction time of 0.5 s (=pulse repetition period). MeAc = butanone, Ac_2 = hexane-2,5-dione. Acetone concentration 2.77 mol/m³, other concentrations in 10⁻⁴ mol/m³

<i>T</i>	Me_0	C_2H_6	MeAc	Ac_2	CH_4	CH_2CO
768 K	42.9	18.5	2.67	~0.2	6.8	3.4
	8.5	3.14	1.09	~0.1	4.3	3.3
778 K	43.2	18.5	2.94	~0.2	8.6	5.4
	8.65	3.1	1.07	~0.1	6.4	4.9
788 K	42.4	17.8	3.1	~0.2	11.0	7.04
	9.1	3.2	1.4	~0.1	6.9	5.9
c/c_{exp}		1.1	1.27		0.9	1.1

TABLE 2

Rate constants resulting from the kinetic modelling. Notation as in Figure 3. Activation energies are in kJ/mol. E_{Me} is taken from Ref. 13, for E_{Ac} see text. The high pressure limit of $k_{2\text{Me}}$ would be slightly larger than our assumed value;^{3,14} it would require about twice the density we employed

	This work	Previous work	Rev.
$k_{2\text{Me}}/10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	25 ^a	~25	10, 11, see also 3, 12
$k_{\text{MeAc}}/10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	46		
$k_{2\text{Ac}}/10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	5.6		
$k_{\text{Me}}/10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$1.1 \cdot \exp(-40/\text{RT})$	$0.53 \exp(-40/\text{RT})$	3, 13
$k_{\text{Ac}}/10^{12} \text{ s}^{-1}$	$69 \cdot \exp(-155/\text{RT})$		
$k_{\text{MeAc}}/(k_{2\text{Ac}}k_{2\text{Me}})^{1/2}$	3.7	2	2, 3
$k_{\text{Ac}}/\sqrt{k_{2\text{Ac}}^c}$	$30 \cdot \exp(-155/\text{RT})$	$1.6 \cdot \exp(-155/\text{RT})^b$	2

^a Not varied.

^b Converted to our adopted activation energy of 155 kJ/mol.

^c $10^9 (\text{mol s m}^{-3})^{1/2}$.

The smallest of these ratios (3.7) does not deviate too much from Brinton's values (1.5 to 2.5) and from collision theory. However we found in all our fits a much larger ratio $k_{\text{Ac}}/(k_{2\text{Ac}})^{1/2}$ than Brinton. The origin of this discrepancy is not clear.

Our temperature range was not large enough to determine the activation energy E_{Ac} for the decomposition of the acetyl radical. So we first adopted Brinton's value of 171 kJ/mol determined from the temperature dependence of $k_{\text{Ac}}/(k_{2\text{Ac}})^{1/2}$. However, evidence that another E_{Ac} had to be chosen was inferred from an analysis of the dark reaction: The thermal bulk reaction (1) can be described by a first order rate equation (AcH = acetone concentration):

$$d \text{ AcH} / dt = k_1 \text{ AcH} \quad (9)$$

in which

$$k_1 = 2.5 \cdot 10^{15} \text{ s}^{-1} \exp(-291 \text{ kJ/mol}/\text{RT}) \quad (10)$$

is established³ over 770 to 1090 K above 130 mbar (that is a slightly higher density than we had).

Such kinetic behavior can easily be understood³ by the assumption that the formation of butanone-2 (MeAc) is the dominant chain termination step, whereas either reaction (2) or (2a) is the initiation.

Like (2), (2a) also results in two methyl radicals, since (3) will be much faster than (2a). Denoting by k_{AcH} either k_2 or k_{2a} , one finds³

$$k_{\text{AcH}} = k_1^2 k_{\text{MeAc}} / (k_{\text{Me}} k_{\text{Ac}}) \\ = 3 \cdot 10^{17} \text{ s}^{-1} \exp(-370 \text{ kJ/mol/RT}) \quad (11)$$

using our constants of Table 2. The activation energy is marginally satisfactory for reaction (2a). (The CC bond energy in acetone has been estimated to 333 kJ/mol³). The preexponential factor is very large. It has the same order of magnitude as the largest values ever found for decay into two fragments, like e.g., for the CC bond splitting in C_2H_6 ^{6,7} or C_2Cl_6 .⁷ Such magnitudes have been interpreted by a transition state with increased entropy, caused by additional low frequency modes.⁶ In the absence of such an effect the preexponential factor is expected to be 10^{12} to 10^{14} s^{-1} for a decomposition into two fragments and 10^{16} to 10^{18} s^{-1} for decomposition into three fragments.³ The numbers of Eq. (11) thus suggest to consider reaction (2) as an example of a triple fragmentation. In this case however it is certainly better to choose instead of $E_{\text{AcH}} = 370 \text{ kJ/mol}$ the thermodynamic enthalpy of reaction for E_{AcH} . From the JANAF tables⁸ one finds ($E_{\text{AcH}} =$) $\Delta H = 387 \text{ kJ/mol}$. This value in turn implies $E_{\text{Ac}} = 155 \text{ kJ/mol}$, which we have adopted in Table 2 instead of Brinton's value of 171 kJ/mol. Then

$$k_2 = 3.8 \cdot 10^{18} \text{ s}^{-1} \exp(-387 \text{ kJ/mol/RT}) \quad (12)$$

The rate of decay into two fragments can either be estimated to

$$k_{2a} \cong 10^{12} \text{ to } 10^{14} \text{ s}^{-1} \exp(-333 \text{ kJ/mol/RT}) \quad (13)$$

or be assumed to be equal to (11). With these rates the direct decay into 3 fragments is predicted to be faster than the stepwise decay above about 505 K, 615 K or 800 K, respectively. Obviously at such high temperatures the direct reaction (2) either dominates (as we assume) or at least is not negligible as initiation.

Figure 4 compares the experimental data corrected according to Table 1 with calculated yields. The best agreement is attained if the absorption cross section σ (relating the initial methyl concentration Me_0 with the energy density ϕ) is assumed to be $1.3 \cdot 10^{-20} \text{ cm}^2$. This σ should be compared with the $2.5 \cdot 10^{-20}$ found by transmission of the laser at 788 K. Since the evaluation of Me_0 from the other concentrations is subject to errors and since the laser was not absorbed

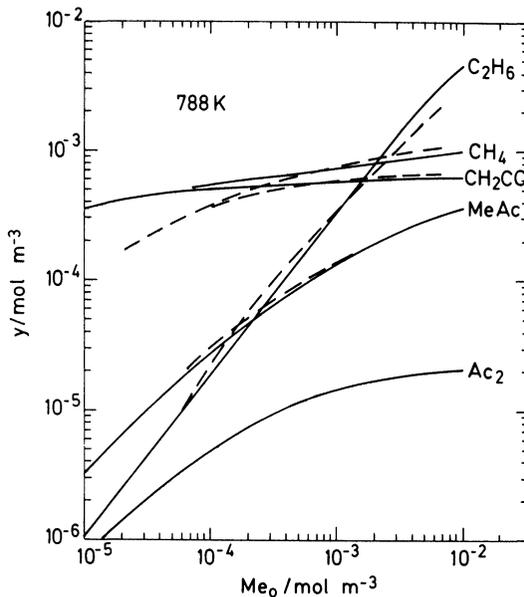
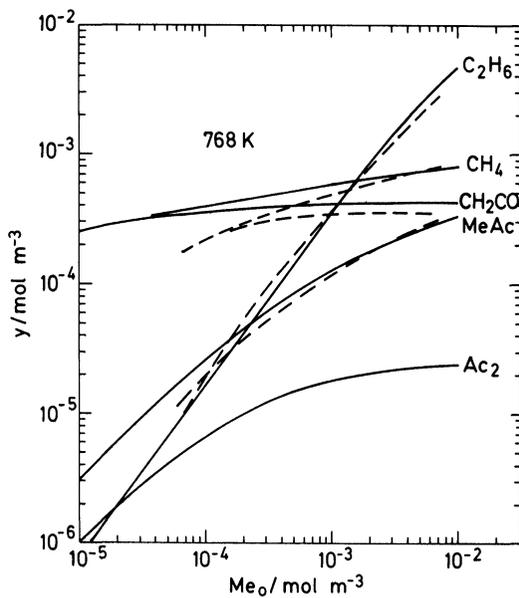


FIGURE 4 Calculated yields (solid lines) fitted to experimental yields (broken lines) as functions of the initial methyl concentration, Me_0 . The experimental yields are from Figure 2, assuming $\text{AcH} = 2.77 \text{ mol m}^{-3}$ and $\sigma = 1.3 \cdot 10^{-20} \text{ cm}^2$ in Eq. (4) and applying the correction factors of Table 1.

very strongly, the agreement seems reasonable. Another reason of the deviation could be the decrease of the cell transmission probably caused by a deposit on the cell windows after some use: If this decrease was much stronger on the entrance than on the exit window, the absolute number of photons in the cell could have been larger than assumed. (Energy was measured behind the cell.) Since the kinetic data only depend on the product $\sigma\phi$, the pertinent σ may be too small. The agreement of calculated and corrected experimental yields is very good down to about 1 mJ/cm^2 ($M_{e_0} \cong 1 \text{ mol/m}^3$), i.e., to 10 times smaller energies than used in the fit. As already mentioned, the deviations at lower energies appear because the subtraction of the dark reaction from experimental yields is an overcorrection since it takes place in a larger volume. If one subtracts only the fraction of the dark reaction occurring in the non-irradiated volume, whereas the other fraction is included in the calculation, the agreement becomes much better. This is an indication that our constants are good enough at least for our purpose: to extrapolate the reactions to lower energies, different pressures and probably also to higher temperatures. However the absolute values of the constants are probably also reasonable, although they are derived from overall yields only. This is indicated by k_{Me} , which was included in the variation and was found to deviate from previous values by only a factor of two (Table 2).

OPTIMUM CONDITIONS FOR THE REACTIONS

For a practical application one would like to have high quantum yield, without losing too much thru-put. Both of them rise with temperature, because of the high activation energy E_{Ac} of the reaction step forming ketene. However, ketene tends to decompose above about 700 K. Photochemical initiation allows us to lower the temperature compared to the thermal case, the lower limit being associated with E_{Ac} . So let us investigate if we can avoid the ketene decomposition at a relatively low temperature. The dark reaction will be neglected for this calculation.

According to Ref. 4 the rate of ketene decomposition has a second-order dependence on the initial pressure. From their data we derive

$$k_{Ket} \cong 1.6 \cdot 10^6 \exp(-147 \text{ kJ/mol/RT}) \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (14)$$

For small conversion u (% of acetone) we can write

$$d \text{Ket} / dt = \dot{u} \text{AcH} - k_{\text{ket}} \text{Ket}^2 \quad (15)$$

AcH and Ket are the acetone and ketene concentrations, as before, and \dot{u} is the relative conversion per second. The solution of (15) is

$$\begin{aligned} \text{Ket} &= (\dot{u} \text{AcH} / k_{\text{ket}})^{1/2} \tanh [(\dot{u} \text{AcH} k_{\text{ket}})^{1/2} t] \\ &\cong \dot{u} \text{AcH} t (1 - \frac{1}{3} \dot{u} \text{AcH} k_{\text{ket}} t^2) \end{aligned} \quad (16)$$

The second term in the parenthesis is the relative loss of ketene by decomposition. If we postulate that it should be smaller than 0.1 even if the conversion $\dot{u}t$ is of the order of 1 (Eq. (16) does not apply for high conversions, but this calculation should only give the order of magnitude), then one needs

$$\dot{u} \geq \frac{1}{0.3} k_{\text{ket}} \text{AcH} \quad (17)$$

Obviously one should either try to make high relative conversion rates (e.g., at high temperature), or one should work at low acetone pressure. To find out numerical values and decide if they would be acceptable, we solved the rate equations (excluding ketene decomposition; the dark reaction was negligible) at 788 K (Figure 5). We also assumed a fixed average intensity of irradiation of 0.5 mW/cm² (5 pulses/s, 0.1 mJ/cm² each). A much smaller intensity would require too large windows and other optics, a higher one would reduce the quantum yield. At a fixed intensity, the initial methyl concentration is proportional to AcH; that is why the quantum yield drops at high pressures. Condition (17) requires to work above or to the left hand side of the broken line in Figure 5; i.e., acetone at densities below 0.5 mol/m³ (12.5 mbar at room temperature). The corresponding conversion rate \dot{u} is $6 \cdot 10^{-4} \text{ s}^{-1} = 2.2 \text{ h}^{-1}$. Both numbers are too small for practical purposes. Therefore it would be interesting to investigate whether they are improved at higher temperature.

For this purpose we can assume continuous irradiation. This is a sufficient approximation at the low intensities and densities (small reaction rates compared to pulse rates) of interest. Let us further assume that the only chain termination of importance is the combination of methyl with acetyl to form butanone. This is good enough to give the scaling laws, as shown by the computer calculation; but

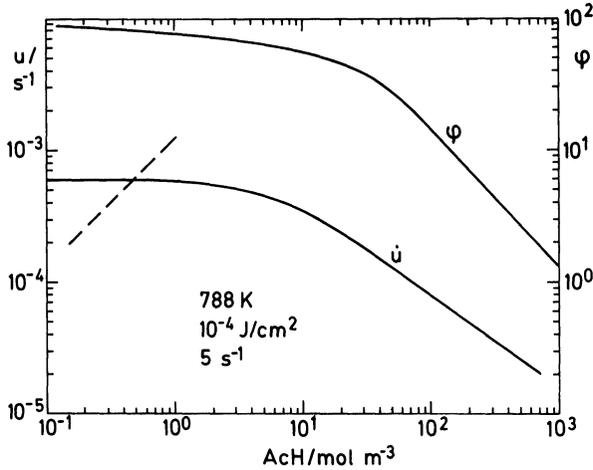


FIGURE 5 Calculated relative conversion rates of acetone, \dot{u} , (see Eq. (15)) and quantum yields, ϕ , for different initial acetone concentrations, AcH. For a given average intensity (0.5 W/cm^2) the figure remains unchanged for lower pulse energies and higher repetition rates than indicated. To avoid decomposition of ketene, one has to work on the left-hand side of the broken line, according to the inequality 17.

the numerical factors should be taken from the latter. Initially the dark reaction will also be neglected. The steady state analysis gives

$$\dot{u} = \frac{1}{\text{AcH}} \frac{d \text{Ket}}{dt} = (k_{\text{Me}} k_{\text{Ac}} \sigma I / hf k_{\text{MeAc}})^{1/2}$$

$$= 1.2 \cdot 10^5 \text{ s}^{-1} \exp(-97.5 \text{ kJ/mol/RT}) \sqrt{I / \text{W cm}^{-2}} \quad (18)$$

(preexponential factor from full numerical calculation). Note also that the quantum yield

$$\phi = \dot{u} / (\sigma I / hf)$$

$$= 7.5 \cdot 10^6 \exp(-97.5 \text{ kJ/mol/RT}) / \sqrt{I / \text{W cm}^{-2}} \quad (19)$$

(preexponential factor from full calculation).

Both \dot{u} and ϕ increase slightly with temperature, as desired. However, due to its larger activation energy (147 kJ/mol), the ketene decomposition increases faster. To reduce it, the acetone density must be further decreased, according to (17).

Another possibility is to increase both the temperature and the intensity in such a way as to keep ϕ constant. Inserting I from Eq.

(19) into (18) we find

$$\dot{u} = \phi^{-1} \cdot 9.0 \cdot 10^{11} \text{ s}^{-1} \exp(-195 \text{ kJ/mol/RT}) \quad (20)$$

Then the maximum acetone density is inferred from (17):

$$\begin{aligned} \text{AcH} &\leq 0.3u/k_{\text{Ket}} \\ &= \phi^{-1} \cdot 1.69 \cdot 10^5 \text{ mol m}^{-3} \cdot \exp(-48.5 \text{ kJ/mol/RT}) \end{aligned} \quad (21)$$

This density now indeed increases with temperature, however only slightly. For example at 873 K it is just a factor of two larger than for continuous irradiation at 788 K and a factor of 4 larger than in Figure 5. Its value (2 mol/m^3) corresponds to 150 mbar at this temperature. The conversion rate is then $1.8 \cdot 10^{-2} \text{ s}^{-1}$ with a quantum yield of 100.

Whereas these numbers are already worth discussing, it has to be noted that the dark reaction (neglected in the above analysis) increases very rapidly with temperature, according to Eq. 10, and becomes just about equal to the quoted photochemical rate at 873 K.

CONCLUSION

Compared to the thermal process, the photochemical reaction can be performed at a lower temperature, the conversion can be driven nearly to completion, the ketene decomposition can be suppressed to a large extent, and the quantum yields can be as large as 100 to 300. The latter two points however require low acetone densities ($1 \dots 2 \text{ mol/m}^3$). While such densities would also have advantages for the kinetics and the temperature equilibration time in the thermal process, they are not attractive from a technical point of view. Low pressure and high conversion would also require an elucidation of the role of two neglects made: the monomolecular part of the ketene decomposition, which seems important at low densities,⁴ and the radical scavenging properties of ketene.

The temperature decrease and quantum yield achieved by us is much smaller than in the case of vinyl chloride production studied in Ref. 1. The reason is certainly the high activation energy for acetyl decomposition. It is about twice as large as the corresponding quantity in the vinyl chloride process. This rate is a bottleneck for the chain, limiting the chain length. Activation energies for the chain steps below about 100 kJ/mol would be much more attractive.

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