KrF Laser Induced Telomerization of Bromides with Olefins. Part 1: Self-Inhibition and Kinetic Analysis

Zhang Linyang*), W. Fuß, and K. L. Kompa

Max-Planck-Institut für Quantenoptik, D-8046 Garching, Federal Republic of Germany

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The chain reaction of several organic bromides with olefins was induced by a KrF laser. In all cases we found a self-inhibition, leading to a termination of first order in the radical concentration. There is indirect evidence that it is due to molecular bromine, accumulated during the reaction in spite of the presence of olefins. It has not been noticed previously. We show that kinetic analysis is easy also for pulsed excitation, and the example $CF_3Br + C_2H_4$ is studied in detail. We found rate constants for $CF_3 + C_2H_4 \rightarrow CF_3C_2H_4$ (7.2 $\cdot 10^9$ cm³ mol⁻¹ s⁻¹; this is in between two previous values) and for $CF_3C_2H_4 + CF_3Br \rightarrow CF_3C_2H_4Br + CF_3$ (1.2 $\cdot 10^9$ cm³ mol⁻¹ s⁻¹) as well as preliminary values for some other reactions.

A. Introduction

Telomerization is an end group dominated polymerization leading to molecules of short chain length. The kinetic chain length can be much larger because of chain transfer reactions (Eq. (3) below). Usual telomerizations are radical reactions. They can be induced photochemically. A wide variety of such reactions has been compiled in a monograph [1]. The insertion of one or several ethylene units into the C-Br bond or organic bromides is one example of them. Usually it is assumed [1-3] that the chain termination is of second order in the radical concentration, while the propagation is of first order, according to the simple reaction scheme:

 $RBr + h\nu \longrightarrow R + Br$ (initiation) (1)

 $R_n + C_2 H_4 \longrightarrow R_{n+2}$ (propagation) (2)

 $R_n + RBr \longrightarrow R_nBr + R$ (chain transfer) (3)

 $X + X' \xrightarrow{(M)} XX'$ (termination). (4)

Here R denotes any radical, the subscript is the number of C atoms, and X denotes R or Br.

Generally in the case of second-order termination, the chain length is proportional to $[R]^{-1}$. Thus it can be increased by distributing the photons over a volume as large as possible. This is especially easy with a laser: Using a wavelength with a large penetration depth, one can profit from the laser's spatial collimation. This principle has been introduced by Wolfrum and coworkers [4]. It might seem a disadvantage to use for this purpose a pulsed light source like an excimer laser, since the temporarily high radical concentrations would favor radical dimers. If however [R] is chosen small enough so that the dimerization takes longer than the time between pulses, there will be no difference to initiation by a continuous light source. To vary [R], we did not vary the wavelength, but we attenuated the laser and

used a short irradiation cell. This is sufficient for analytical purposes.

Initially we studied the reaction of ethylene with BrC₂F₄Br, because the products are of some technical interest. The results will be presented in part 2 of this investigation [5]. But in this case we found many kinetic complications, not consistent with the simple scheme (1)-(4), including also a self-inhibition of the reaction which is of first order in the radical concentration. Therefore we reinvestigated for comparison the simpler system of $CF_3Br + C_2H_4$, which was previously studied and analysed assuming second-order termination [1,2]. Also here we found a first-order termination of self-inhibition type. It is probably due to molecular bromine, accumulated during the reaction, in spite of the presence of olefins. If not removed, it decreases the quantum yields, and it makes the decrease of [R] useless. We found the same small quantum yield as with the laser, when we used a low intensity light source (a Xe arc lamp with filter) to initiate the reaction. Previously this self-inhibition has not been noticed in the reaction of olefins with bromides [1, 2] or iodides [1, 3].

The contribution of a first-order termination was proven by comparing the experimental results with a kinetic analysis. Whereas such an analysis has long been known for continuous or chopped light sources [7], it was not available for single-pulse light sources like the KrF laser. We show that it is easy to carry out also for this case. In part 2 [5], it is used to prove two further unexpected phenomena.

All reactions were performed in gas phase. The yields of the end products were analyzed by gas chromatography combined with a mass spectrometer.

The following two sections present experimental details and experimental results together with results of numerical calculations. The kinetic analysis (sec. D) is divided into several parts: Sec. D1-3 show how the dependence of yields on laser energy (i.e. on initial radical concentration) is influenced by the type of termination; sec. D4 compares these predictions with the measured data and presents more arguments for the self-inhibition; sec. D5 then analyses the dependence on concentrations of reactants and presents the rate constants finally used. Sec. E summarizes the results and gives some further conclusions.

^{*)} Home address: University of Science and Technology of China, Hefei (Anhui), P. R. China.

B. Experimental

The KrF laser emitted pulses with 20 ns duration and 248.3 nm wavelength. It was operated at a repetition rate of 1 s^{-1} . When attenuation was desired, we used quartz glass of infrared quality. Before entering the irradiation cell, we cut the beam ($\approx 12 \cdot 35 \text{ mm}^2$) by a diaphragm to $12 \cdot 24 \text{ mm}^2 = 2.8 \text{ cm}^2$ in order not to hit the wall.

The irradiation cell consisted of quartz glass with a teflon valve. It had 28 mm inner diameter, 100 mm length and 65 cm³ volume. Since diffusion was slow enough during the reaction time, the reaction volume, used in the calculations, was identical with the irradiated volume (28 cm³). For a few irradiations we used also a cell with 170 cm³ volume, 46 mm diameter and 100 mm length.





Product yields y as functions of initial radical concentration $[\mathbf{R}]_0$ or laser pulse energy E and of reactant concentrations. Concentration units refer to the irradiated volume, not to the cell volume

Penetration depths of the light were always sufficient to illuminate the full length of the cells. The extinction coefficient of CF_3Br at 248 nm is $2 \cdot 10^{-21} \text{ cm}^2 = 0.051 \text{ cm}^{-1} \text{ base e}$.

The gases CF₃Br (Matheson, 99%) and C₂H₄ (Linde, 99.8%) were used without further purification. The products were analysed by a gas chromatograph combined with a mass spectrometer (Hewlett-Packard GC 5890 with MS 5970). As a column we used a 0.2 mm \cdot 25 m capillary coated with 5% phenyl-methylsilicone. Temperature program: 30° for 2 min, then heating by 5 K/min until 200°. Retention times and characteristic mass numbers will be published in a laboratory report [6]. For the mass spectrometer sensitivity (total ion current for mass range 23 to 800) for the various compounds we assumed group additivity: The relative response for some calibration compounds was well represented by the sum of contributions of 0.25, 0.40 and 1.00 for Br, CF₃ and C₂H₄ groups respectively. This method is probably accurate to within 10%.

Using these relative responses, we determined the product quantities relative to CF_3Br from the integrated gas-chromatographic signals. The conversion of CF_3Br was then calculated from the sum of products. We assume that products not detected (e. g. C_2F_6 , which was not separated from the air peak, or less volatile products, deposited on the cell wall) can be neglected. The calculations confirm this assumption. Irradiation times were chosen so, that the total conversion was always about 30% of the irradiated volume (15% of the cell volume). (At much smaller conversion the self-inhibition is more difficult to observe, although even then it cannot be neglected: see Fig. 4 below.) The individual conversions per pulse which we give should be understood as averages over the irradiation time. Actually they decreased with pulse number (see sec. D4).

C. Results for $CF_3Br + C_2H_4$

Figs. 1a-c show product yields as a function of reagent pressures and of the initial radical concentration $[R]_0$. The latter is proportional to the laser pulse energy. The solid lines are from numerical calculations (sec. D5). Quantum yields can be deduced from these figures by dividing the yields over the initial radical concentration, which is also shown. From the logarithmic slopes of the energy dependences (Fig. 1a) we can deduce the kinetic order of the termination reaction, without knowing mechanistic details. This is shown for various orders in sec. D1-3 and applied to our case and discussed in sec. D4. Sec. D5 rationalizes also the other dependences and sketches the quantitative calculations.

D. Kinetic Analysis

The analysis will finally be done by numerical integration of the rate equations. But an initial overview and an initial set of constants can be received using two approximations, which are in common use:

- Assume steady-states for *ratios* of radical concentrations. (This assumption is verified by numerical calculations for all radicals but one. See sec. D5.)
- Assume that the rate constant for termination (radical combination) is the same for all radicals.

Then only the total concentration of radicals [R], has to be calculated as a function of time (see sec. D1-3). The yield y_p of a product P produced in a first-order step during a long time after the laser pulse is then

$$y_{\rm p} = a_{\rm p} \int_0^\infty [\mathbf{R}] \,\mathrm{d}t \,. \tag{5}$$

The propagation frequencies a_p are time independent and contain, apart from rate constants, only ratios of radical concentrations. They will be derived by a steady-state analysis in sec. D5. Whereas a_p will depend on details of the reaction scheme, the integral in (5) will be determined entirely by the reactions removing the radicals. (The generation of the radicals can be considered a temporal delta function.) So the second factor of (5) will be considered first (sec. D1-3). The laser energy dependence of this factor alone permits to deduce the type of termination (sec. D4).

A time-averaged kinetic chain length can be defined by

$$v_{\rm p} = y_{\rm p} / [\mathbf{R}]_0 \tag{6}$$

where $[R]_0$ is the initial radical concentration. Actual chain lengths vary with [R] and thus with time. Quantum yields are equal to v_p in our case, since the quantum yield of the primary photodissociation of bromides can be assumed to be 1.

1) First-Order Termination

This is usually caused by some inhibitor Inh, present as an impurity, which converts the radicals R into some inert form. (In [R] only the active radicals are included.)

$$E + Inh \rightarrow R-Inh (k_1)$$
 (7)

Defining $a_I := k_I$ [Inh], we get for the radical concentration and its temporal integral (5):

$$[\mathbf{R}] = [\mathbf{R}]_0 \exp(-a_{\mathbf{I}}t) \tag{8}$$

$$y_{\rm p} = a_{\rm p} [\mathbf{R}]_0 / a_{\rm I} \tag{9}$$

$$v_{\rm p} = a_{\rm p}/a_{\rm I} \,. \tag{10}$$

So in this case the product yields are proportional to the initial radical concentration $[R]_0$ (so to the laser pulse energy) and the chain length does not depend on $[R]_0$.

2) Second-Order Termination

This is the most common termination type for radical chain reactions.

$$\mathbf{R} + \mathbf{R} \to \mathbf{R}_2 \quad (k_t) \tag{11}$$

Then

$$[\mathbf{R}] = ([\mathbf{R}]_0^{-1} + 2k_t t)^{-1}$$
(12)

The integral (5) diverges in this case. If however $k_t[\mathbf{R}]_0 \gg t_{rep}^{-1}$, the repetition rate, then after a time t_{rep} the initial concentration $[\mathbf{R}]_0$ is restored by the laser pulse and the integration should be performed until t_{rep} . (This was the case in all our experiments.) Then

$$y_{\rm p} = a_{\rm p} (2k_{\rm t})^{-1} \ln(1 + 2k_{\rm t} t_{\rm rep} [{\rm R}]_0)$$
(13)

$$v_{\rm p} = a_{\rm p} (2k_{\rm t}[{\rm R}]_0)^{-1} \ln(1 + 2k_{\rm t} t_{\rm rep}[{\rm R}]_0) \,. \tag{14}$$

So for high $[\mathbf{R}]_0$ the product yields nearly do not depend on the laser pulse energy, and the quantum yields (chain lengths) are approximately proportional to $[\mathbf{R}]_0^{-1}$. So at high pulse energies, the energy dependence is an easy means to distinguish between first and second order termination, and the difference is quite distinct. At lower energies, if the recombination is only very incomplete between two pulses, one should apply the kinetic analysis like for continuous irradiation. In this case, as is well known [7], $y_p \propto I^{1/2}$ (*I* is the average intensity of irradiation).

The change from I^0 to the $I^{1/2}$ dependence occurs just when $k_t \cdot t_{rep} \cdot [\mathbf{R}]_0 = 1$. In such a way one can find out k_t . This has been done e.g. in [8]. The method is a little bit related to the rotating-sector method [7].

For first order termination such an inflection of $y_p(I)$ or $v_p(I)$ does not exist. The chain length is independent of the average intensity throughout.

3. Mixed First and Second Order Termination

In this case the reactions (7) and (11) both consume the radicals. Then one must solve the differential equation

$$-d[\mathbf{R}]/dt = a_{I}[\mathbf{R}] + 2k_{t}[\mathbf{R}]^{2}.$$
(15)

With the abbreviation

$$r := 2k_{\rm I} [\mathbf{R}]_0 / a_{\rm I} \tag{16}$$

we find for the radical concentration and its temporal integral

$$[\mathbf{R}] = [\mathbf{R}]_0 / (-r + (1+r) \exp(a_1 t))$$
(17)

$$\int_{0}^{\infty} [\mathbf{R}] dt = ([\mathbf{R}]_{0}/a_{1}) r^{-1} \ln(1+r)$$
(18)

and for products of the inhibiting reaction

$$y_{\rm I} = [R]_0 r^{-1} \ln(1+r) \tag{19}$$

$$v_1 = r^{-1} \ln(1+r) \,. \tag{20}$$

Yields of products of other first-order reactions are proportional to these expressions:

$$y_{\rm p} = (a_{\rm p}/a_{\rm I}) y_{\rm I} \tag{21}$$

$$v_{\rm p} = (a_{\rm p}/a_{\rm I}) v_{\rm I} \,.$$
 (22)

These relations transform to those of case 1) in the limit of negligible second-order reaction ($r \ll 1$). They also contain case 2), if t_{rep} is suitably chosen.



Fig. 2

Relative quantum yields v of first-order and second-order products as a function of the ratio of termination rates, calculated by Eqs. (20) and (24). The abscissa can also be understood as $[R]_0$ in units of $a_1/2k_t$. The broken lines are $v \cdot r$, i.e. the yields (Eqs. (19) and (23)) in units of $a_1/2k_t$.

The function $v_1(r)$ is shown in Fig. 2. Comparing it with the measured energy dependence of v_p of any (first-order) product or of the total conversion, one can determine r, the relative rates of first- and second-order terminations. It is even sufficient to find the places where the logarithmic slopes are equal in the two figures (Fig. 2 and the measured v_p as function of $[\mathbb{R}]_0$) and then insert the abscissa value $[\mathbb{R}]_0$ (experimental figure) into the the abscissa value read on Fig. 2. This is done for our case in the next section.

The yield of recombination product results from material balance:

$$y_{RR} = 0.5 ([R]_0 - y_1)$$

= 0.5[R]_0 (1 - r^{-1} ln(1 + r))
$$\begin{cases} = 0.5 k_1 [R]_0^2 / a_1 \text{ for } r \ll 1 \\ = 0.5 [R]_0 \text{ for } r \gg 1 \end{cases} (23)$$

$$v_{\rm RR} = 0.5 \left(1 - r^{-1} \ln(1+r)\right). \tag{24}$$

This function is also shown in Fig. 2. y_{RR} is proportional to $[R]_0$ at high $[R]_0$, while only at low energy it is $\propto [R]_0^2$. (For pure second-order termination, if the termination rate is fast compared to the pulse repetition rate, there is always $y_{RR} \propto [R]_0$, since there is no competing loss of radicals. For first-order termination there is of course no y_{RR} .)



Quantum yields φ of total conversion of several bromides (in reaction with olefins) as functions of the initial radical concentrations [R]₀. To calculate the conversions, multiply by the abscissa

4) Observed Type of Termination

Fig. 3 shows the conversion of starting bromides as a function of laser energy. The logarithmic slopes are intermediate between 1 (first-order termination) and 0 (second-order termination). Comparison of the slopes with Fig. 2 yields a first-order contribution of $a_{\rm I} \approx 1440 \, {\rm s}^{-1}$ for the case of CF₃Br + C₂H₄, if we assume a second-order rate constant of $k_{\rm t} = 3 \cdot 10^{12} \, {\rm cm}^3 \, {\rm mol}^{-1} \, {\rm s}^{-1}$, which is the lower of the reported values for CF₃[8]. (Larger radicals tend to combine a little bit more slowly than smaller ones.) We interpret the first-order terminations as an inhibition (see below).

We found that a_1 does not depend on the olefin pressure and in the case of BrC_2F_4Br is independent of the bromide pressure. So the inhibition cannot be due to an impurity in these gases. Since most of the experiments were done at relatively high pressure (several hundred mbar), it cannot be due to wall effects either. a_1 was 3 times smaller, when in some experiments we used a 3 times larger cell (see the data with bromide + ethylene + tetrafluoroethylene in Fig. 3, curves 1 and 2). This indicates that the inhibitor is a side product of the reaction itself: After each pulse it dilutes from the irradiated volume by diffusion over the cell volume. The fact that it occurs for all the bromides of Fig. 3, indicates that this side product may be Br_2 or a reaction product of it. 0.1 mbar of Br_2 would be sufficient to explain the size of a_1 , using the known reaction rate constant of $CF_3 + Br_2$, $k_1 = 3 \cdot 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [9]. At a given bromide pressure, the accumulated quantity should be approximately constant, because we worked with always nearly the same conversion (15%) of the bromide. For changing bromide pressure, the accumulated Br_2 should also increase to some extent, as nearly always observed, unless another accumulated product (C_2F_4 in the case of BrC_2F_4Br [5]) can scavenge it. In an initial attempt to scavenge the bromine by copper wire, the removing was apparently not fast enough to compete with the pulse repetition rate.



Conversion of BrCF₂CF₂Br (mixed with C₂H₄) as functions of the number of pulses s. x = accumulated conversion, $\bar{y} =$ average conversion = $-s^{-1} \ln(1-x) [BrCF_2CF_2Br] V_{cell}/V_{irrad}$, y = instantaneous conversion = $(dx/ds) [BrCF_2CF_2Br] V_{cell}/V_{irrad}$

A clear proof that the inhibitor is an accumulated product, comes from the dependence on the number of pulses (Fig. 4). Obviously after 50% total conversion the fractional conversion per pulse is decreased by more than an order of magnitude. This decrease is not due to consumption of reagents, as we know from the dependence on bromide and olefin pressures (Fig. 1b and c). It is also not due to secondary photolysis of products, because the latter have a 4 times smaller absorption cross-section than the starting bromide BrC_2F_4Br . (This is the reason why we show this bromide in Fig. 4 instead of CF_3Br . The absorption cross-section of the latter is 2 times smaller than that of the products. But even in this case, secondary photolysis would not regenerate the starting materials.)

We did not expect accumulation of molecular bromine in the presence of several hundred mbar of an olefin. The reaction of Br with C_2H_4 is fast $(1-4 \cdot 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ with an activation energy of 0-12 kJ/mol [9,10]). Then the BrC_2H_4 radical should easily scavenge another Br atom to form BrC_2H_4Br . The latter bromide has no special inhibiting effect, as we found by adding it to the reaction system. On the other hand the decomposition of the radical to $Br + C_2H_4$ should also be very rapid, since it is endothermic by only 33 kJ/mol [10]. This rate can be estimated to be larger than 10¹³ exp(-45 kJ mol⁻¹/RT) s⁻¹ = 10⁵ s⁻¹. So the scavenging of Br atoms will not be efficient under our conditions. Evidence for nearly complete dissociation of BrC_2H_4 comes from an experiment in which we irradiated $BrC_2H_4Br + C_2F_4$: In this case we did nearly not observe any product containing a BrC_2H_4 end group.

It is even more surprising that addition of tetrafluoroethylene to the mixture did not completely scavenge the bromine either. This fluorinated olefin forms a strong bond (81 kJ/mol [11]) already with the first bromine atom, so that back-dissociation will not be noticeable. In this case we suggest that Br_2 is formed in competition with formation of BrC_2F_4Br :

$$\mathbf{BrC}_{2}\mathbf{F}_{4}\mathbf{Br}$$
 (25)

$$\mathbf{Br}\mathbf{C}_{2}\mathbf{F}_{4} + \mathbf{Br} \mathbf{F}_{2} + \mathbf{C}_{2}\mathbf{F}_{4}$$
(26)

The second channel is exothermic by about 100 kJ/mol and probably fairly efficient. Of course a similar channel is also conceivable for C_2H_4 . It can be considered to be the second step of a three-body recombination: $2Br + \text{olefin} \rightarrow Br_2 +$ olefin. The bromine molecules formed in this way can later combine again with the olefin, especially at the wall. In fact we have some indication that the yield of BrC_2H_4Br depended on the condition of the wall.

The concentration of Br_2 was too small to be detected by the eye or by a UV spectrometer. However in an analogous experiment with $CF_3I + C_2H_4$ or C_2F_4 , the molecular iodine formed was easily recognized by its violet color. In one experiment we also added 4 mbar Br_2 to 200 mbar $CF_3Br +$ 400 mbar C_2H_4 . Although the Br_2 colour disappeared within seconds, the quantum yield of CF_3Br consumption decreased from 5 (without added Br_2) to 1.8.

For every radical scavenged by Br_2 one Br atom is released. If e.g. 50% of these atoms can form BrC_2H_4 and if this radical can efficiently contribute to the chain reaction by means of a Br atom transfer

$$BrC_2H_4 + RBr \rightarrow BrC_2H_4Br + R$$
 (27)

then the inhibition effect would be reduced by these same 50%. In fact we have some indication [5] that such a chain transfer occurs, if $RBr = BrC_2F_4Br$. However with CF_3Br this reaction is probably too inefficient.

In [3] the system $CF_3I + C_2H_4$ was irradiated by a lamp. A chain length of 200 was reported. It was determined from the product ratio $CF_3(C_2H_4)_nI/C_2F_6$. (This is correct, if there is only a second-order termination.) The quantum yield was not measured. We considered it conceivable that the visible and near UV part of the lamp spectrum might have photolysed the accumulated I₂, thus enhancing its addition to the olefin and reducing the self-inhibition effect. We checked this idea, using a xenon arc lamp (500 W electric power). To avoid heating of the cell, we reduced the long-wavelength radiation using a mirror which preferentially reflected 248 nm. In the cell this part of the radiation was about 30%with a power density of 0.04 W/cm^2 typically. Using the same gases with the same pressures as in [3] (100 mbar CF₃I + 820 mbar C₂H₄), we found a "chain length" (defined as above) of 165 at a CF₃I conversion of 46%. But the quantum yield for conversion of CF₃I was only 1.6, i.e. even less than for the bromide telomerization, induced by the KrF laser. We also used the laser radiation to initiate the reaction, in addition to the visible and near UV part (isolated by a pyrex glass filter) of the Xe arc lamp emission to destroy the I₂ or Br₂. Compared to pure laser irradiation, there was no strong change of quantum yield for CF₃I + C₂H₄ and for BrC₂F₄Br + C₂H₄. So obviously the photolysis of the halogen molecules does not sufficiently reduce their concentrations.

5) Steady-State Analysis

In this section we derive by steady-state considerations the production rate factors a_p for Eq. (5). Such an analysis not only helps to track which rate is influenced by what and to quickly check an assumed mechanism, but it is also useful to guide the numerical calculations. In the pulsed case, ratios of radical concentrations become stationary, if the propagation reactions are much faster than the termination reactions. This was true for all radicals except one $(CF_3C_4H_8)$, which is less reactive than the others. Since its concentration is small (due to recombination with other radicals), it does not perturb the steady state of the other radicals. Anyway the main purpose of the steady-state analysis is to provide some initial rate constants to insert into the numerical integration of the kinetic equations, which is then optimized to provide the final constants. It even does not matter, if for convenience we assume stationarity for the concentrations themselves instead of for their ratios.

The steady-state analysis is only sketched here, because it is identical to the case of continuous illumination, except for the initiation.

For $CF_3Br + C_2H_4$ we assume the following reaction mechanism:

Initiation:

 $CF_3Br + hv(248 \text{ nm}) \rightarrow CF_3 + Br$

Terminations:

$\mathbf{R} + \mathbf{R}'$	\rightarrow	RR′	(k_t)
R + Br	\rightarrow	RBr	(k_{RB})
Br + Br + M	\rightarrow	$Br_2 + M$	(k_{BB})
$\mathbf{R} + \mathbf{B}\mathbf{r}_2$		RBr + Br	(k_1)

Propagations:

$$CF_{3} \xrightarrow{+C_{2}H_{4}} CF_{3}C_{2}H_{4} \xrightarrow{+C_{2}H_{4}} CF_{3}C_{4}H_{8} \xrightarrow{+C_{2}H_{4}} \cdots$$

$$(k_{2}) \downarrow + CF_{3}Br \qquad (k_{4}) \downarrow + CF_{3}Br$$

$$CF_{3}C_{2}H_{4}Br \qquad CF_{3}C_{4}H_{8}Br$$

$$+ CF_{3} \qquad + CF_{3}$$

The steady-state analysis uses only the propagation reactions. We write down the definition of the total radical concentration [R]

$$[\mathbf{R}] = [\mathbf{CF}_3] + [\mathbf{CF}_3\mathbf{C}_2\mathbf{H}_4] + [\mathbf{CF}_3\mathbf{C}_4\mathbf{H}_8] + \cdots \qquad (28)$$

and then ask for equality of loss and generation rates of the radicals (left and right hand sides of the Eqs. (29) and (30), respectively; radical concentrations in bold type to guide the eye):

$$k_1[C_2H_4][CF_3] = k_2[CF_3Br][CF_3C_2H_4]$$

$$+ k_4[CF_3Br][CF_3C_4H_8]$$
(29)

$$(k_3[C_2H_4] + k_2[CF_3Br])[CF_3C_2H_4] = k_1[C_2H_4][CF_3].$$
(30)

(For $CF_3C_4H_8$ see below.) This set of linear equations can be solved for ratios of radical concentrations.

Since no recombination products of $CF_3C_4H_8$ have been observable, we can neglect this radical in [R]. (We can infer the small concentration of the heavier radical also from the small product ratio $[CF_3C_4H_8Br]/[CF_3C_2H_4Br]$.) So

$$[\mathbf{R}] \approx [\mathbf{CF}_3] + [\mathbf{CF}_3\mathbf{C}_2\mathbf{H}_4].$$
 (31)

The production frequency of $CF_3C_2H_4Br$ is according to definition

$$a_{p}(CF_{2}C_{2}H_{4}Br) = k_{2}[CF_{3}Br] \frac{[CF_{3}C_{2}H_{4}]}{[R]}$$

$$= k_{2}[CF_{3}Br] \left(\frac{[CF_{3}]}{[CF_{3}C_{2}H_{4}]} + 1\right)^{-1}.$$
(32)

The last line follows from (31). The ratio in this line can be resolved by means of Eq. (30):

$$a_{p}(CF_{3}C_{2}H_{4}Br) = k_{2}[CF_{3}Br] \frac{k_{1}[C_{2}H_{4}]}{(k_{1}+k_{3})[C_{2}H_{4}]+k_{2}[CF_{3}Br]}$$

$$\approx k_{2}[CF_{3}Br] \text{ at high } [C_{2}H_{4}] \qquad (33)$$

 $(k_3 \ll k_1 \text{ follows from the small ratio of products CF_3C_2H_4Br to CF_3C_4H_8Br)$. In fact at high ethylene pressures this first bromide product is about proportional to [CF_3Br] (Fig. 1b) and independent of [C_2H_4] (Fig. 1c). From the measured yields we can deduce the production frequency by dividing by $\int [\mathbf{R}] dt$, which is calculated by Eq. (18) from [R]₀ and a_1 ; the latter is known from the previous section. In this way we get a first guess of k_2 . When at lower [C_2H_4] the two terms in the denominator become equal, the dependence on ethylene pressure sets in. From this part of the curve one can get k_1/k_2 , and since k_2 is already known, also k_1 .

According to the computer calculations, stationarity is not reached for $[CF_3C_4H_8]/[R]$. Therefore we omitted the corresponding equation above. It is however interesting to see which conclusions from it are still qualitatively correct.

(34)

It would read (the symbol \approx means here "tentatively set equal")

$$(k_{5}[C_{2}H_{4}] + k_{4}[CF_{3}Br])[CF_{3}C_{4}H_{8}] \approx k_{3}[C_{2}H_{4}][CF_{3}C_{2}H_{4}]$$

from which we would get

$$\frac{[CF_{3}C_{4}H_{8}]}{[CF_{3}C_{2}H_{4}]} \approx \frac{k_{3}[C_{2}H_{4}]}{k_{5}[C_{2}H_{4}] + k_{4}[CF_{3}Br]} \begin{cases} = k_{3}[C_{2}H_{4}]/(k_{4}[CF_{3}Br]) \\ at high [CF_{3}Br] \\ = k_{3}/k_{5} at high [C_{2}H_{4}] \end{cases}$$
(35)

If this ratio would be time independent, it should be identical to $\int [CF_3C_4H_8] dt / \int [CF_3C_2H_4] dt$, which in turn becomes after multiplication by k_4/k_2 equal to the product ratio $[CF_{3}C_{4}H_{8}Br]/[CF_{3}C_{2}H_{4}Br]$. Inspection of Fig. 1b and c shows, that this ratio is proportional to [C₂H₄] and independent of $[CF_3Br]$. So both limiting cases of (35) seem to be fulfilled at the same time. This is not consistent with the prediction. The reason is the non-stationarity: The heavier bromide is formed primarily by termination processes (involving a_1 instead of transfer reactions (involving k_4). Better consistency can be got by substituting a_{I} for k_{4} [CF₃Br] in the equations above. But this is only a phenomenological procedure, to be handled with care. This variant is a correct guide, telling which constant controls the ratios of bromide yields and their dependences on [C₂H₄] and [CF₃Br], and which constant should be varied accordingly in the numerical calculations. For example, if k_5 would be very small, this bromide ratio would strongly depend on [CF₃Br], in contrast to observation. (Note that in this way we can conclude about k_5 , although we did not observe products of this reaction.) It is also natural that no definite value for k_4 can be derived from the analysis, because recombination with Br dominates.

The rate constants guessed in the described way were used for the numerical integration of the kinetic equations. The calculated dependences on $[R]_0$, $[C_2H_4]$ and $[CF_3Br]$ were then compared with the measured ones (Fig. 1a-c). To correct any deviations, we varied just those rate constants, which were suggested by the expressions for the production frequencies like (33) and also (35). This procedure converged after only 3 to 4 attempts.

Let us sketch again the procedure and summarize which constant is derived from what:

- $-k_t = 3 \cdot 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, assumed to be similar or slightly smaller than the dimerization rate for CF₃ [9, 12]. All the following rate constants are proportional to this constant.
- $-k_{BB} = 10^{16} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ assumed. This is about half the value for I + I + C₂H₄ [13]. (Three-body recombinations of Br are usually two times smaller than those of I [13].) It has a negligible influence to the bromide yields.
- $-k_{BR} = 5 \cdot 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from quantum yield of dissociation of pure CF₃Br (≈ 0.8). It can be derived numerically or analytically. We do not present the details, because k_{BR} plays a minor role only.
- $a_{\rm I} = 1440 \text{ s}^{-1}$ (interpreted as $k_{\rm I} [Br_2]$) at $[CF_3Br] = 200 \text{ mbar from comparison of total conversion as a function of <math>[R]_0$ with calculated curves (sec. D4).

- From $k_t[\mathbf{R}]_0/a_1$ and Eq. (18) we calculate $\int \mathbf{R} dt$, by which we divide the experimental yields to get production frequencies which can then be analysed by steady-state considerations.
- $-k_2 = 1.2 \cdot 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ from } \text{CF}_3\text{C}_2\text{H}_4\text{Br}$ yield at high [C₂H₄].
- k_1/k_2 from CF₃C₂H₄Br yield at lower [C₂H₄]. So $k_1 = 7.2 \cdot 10^9$ cm³ mol⁻¹ s⁻¹.
- $k_1 = 7.2 \cdot 10^{7} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$ - $k_3 = 6.0 \cdot 10^7 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$
- $k_3 = 6.0 \cdot 10^7 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$ $k_5 = 6.0 \cdot 10^7 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$

from the ratio of yields of $CF_3C_4H_8Br$ to $CF_3C_2H_4Br$ as a function of $[C_2H_4]$ and $[CF_3Br]$.

 $-k_4 = 1 \cdot 10^5$ cm³ mol⁻¹ s⁻¹ assumed. Yields do nearly not depend on it.

The yields are sensitive, if k_1 or k_2 are changed by more than 20% or k_3 or k_5 by more than a factor of 2. Especially the latter two constants could of course change, if the assumed mechanism is incomplete. That it is probably not quite complete, is indicated by the CF₃C₄H₈Br yields, whose dependence on [CF₃Br] is not reproduced quite satisfactorily by the calculations. In some other bromide + olefin systems, we also found contributions of depolymerisation (radical induced abstraction of C₂H₄) [5].

For k_1 two values have been published previously: 3.3 \cdot 10¹⁰ [9] and 9 \cdot 10⁸ cm³ mol⁻¹ s⁻¹ [3]. The smaller one has been determined considering second-order termination only, the larger one by theoretical calculations. Ours is in the middle of them.

The calculations agree with the observed dependences nearly throughout (Fig. 1a-c). Only the dependence of $[CF_3C_4H_8Br]$ on $[CF_3Br]$ is not quite satisfactorily reproduced. So, the mechanism in general is supported by the calculations, although it is probably not quite complete.

E. Conclusion

We have shown that for pulsed excitation the kinetic analysis is not much more difficult than for continuous excitation. In the analytical considerations the yields are calculated as products of two factors. One of them results from steady-state considerations, which are nearly identical for

pulsed and continuous irradiation. The other is $\int_{0}^{\infty} [R] dt$, if

the product is kinetically of first order in the concentration of any radical, or an integral over another function of [R], for different kinetic order. These integrals have been given for various orders of termination reactions in sec. D1-3. The steady-state analysis yields some initial values, or at least estimations, which are then improved by numerical integration of the rate equations. Comparison of calculated and experimental dependences of yields on concentrations of reagents and on [R]₀ is a critical test of the assumed mechanism. Already without calculation we can quickly recognize from the laser energy dependence (dependence on [R]₀) if two products are formed by reactions of the same kinetic order in radicals: Their yields are parallel in a loglog plot versus laser energy. From the logarithmic slope of the yields versus [R]₀ we can also immediately recognize the kinetic order of the termination: slope 1 means first order in [R], slope near 0 means second order.

For all the investigated laser photolyses of bromides + olefins we found first-order termination of a self-inhibition type, which we ascribe to accumulated molecular bromine. That the inhibitor is accumulated is proven by Fig. 4, and that it is Br_2 is suggested by the observation of the phenomenon for all the investigated bromides. We have to postulate a Br_2 accumulation between 0.1 mbar (for $CF_3Br + C_2H_4$) to 0.7 mbar (for 100 mbar $BrC_2F_4Br + 100$ mbar C_2F_4). Especially the latter observation is surprising, in view of the reactivity of C_2F_4 . This mixture is probably stable only for fractions of a second. We observed the same inhibition also in irradiations with lamps. Although the long wavelengths contained in their spectrum can photolyse the Br_2 , its addition to the olefin is not much accelerated thereby, and the bromine concentration is not much lowered.

The accumulation of bromine must be avoided, if good quantum yields are desired. The best way is probably to remove the reaction mixture rapidly from the irradiation zone and bind the Br_2 with some scavenger (e.g. a reactive metal) or make it react with the olefin using a polar solvent or catalyst. If the first-order termination is effectively suppressed in this way, the quantum yield can be further improved by chosing a smaller radical concentration, e.g. by using a longer wavelength with larger penetration depth. Using a XeCl laser (308 nm) this should even be possible in liquid phase.

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KrF Laser Induced Telomerization of Bromides with Olefins. Part 2: BrC_2F_4Br and $BrC_2F_4C_2H_4Br$ with C_2H_4 and C_2F_4

Zhang Linyang*), W. Fuß, and K. L. Kompa

Max-Planck-Institut für Quantenoptik, D-8046 Garching, Federal Republic of Germany

Chemical Kinetics / Photochemistry / Radicals

We investigated the photochemical insertion of one to three olefin units into a CBr bond of two dibromides in gas phase. Unexpected high quantum yields (up to 30) were found in the system $BrC_2F_4Br + C_2H_4$ for the product $BrC_2F_4C_4H_8C_2F_4Br$ and some others. Therefore they cannot be radical combination products, but must arise from chain propagation. To explain their formation, accumulation of C_2F_4 must be assumed. The addition of ethylene to a radical can be reversed by Br atoms. This reaction strongly influences the product spectrum. Synthesis of $BrC_2F_4C_4H_8C_2F_8Br$ would be economic by the laser method. The preparation of $BrC_2H_4C_2F_4C_2H_4Br$ was also much improved over previous methods.

1. Introduction

Insertion of ethylene or tetrafluoroethylene into the CBr bonds of BrC_2F_4Br gives some products, which can be useful for synthetic purposes due to their bifunctional nature. This insertion is a radical chain reaction, often called telomerization [1]. Its propagation steps consist of the molecule growth and the chain transfer (in this case a Br atom transfer):

$$\mathbf{R} + \mathbf{C}_2 \mathbf{H}_4 \longrightarrow \mathbf{R} \mathbf{C}_2 \mathbf{H}_4 \tag{1}$$

$$\mathbf{R}' + \mathbf{R}\mathbf{B}\mathbf{r} \to \mathbf{R}'\mathbf{B}\mathbf{r} + \mathbf{R} \tag{2}$$

where \mathbf{R} and \mathbf{R}' are radicals. It can be induced by initiators or photochemically. If the termination is (as usual) of second

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^{*)} Home address: University of Science and Technology of China, Hefei (Anhui). P. R. China.