Computerised Pulse-Radiolysis System for Gas-Phase Kinetics

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Pulse-radiolysis equipment for studies of radical reaction kinetics in the gas phase is described. The equipment is built around an accelerator of the Febetron type for 800 keV electrons. The analysing light is pulsed with optical feedback regulation of the intensity to increase the luminosity ca. 50 times during the measurement. It is equipped with photoelectric detection of transient optical absorptions in the time interval 1×10^{-8}–5×10^{-3} s of radicals in the wavelength range 200–900 mm. The stray-light level is low ($<1\%$) even at 200 nm. The data collection system is computerised and controlled by a PC with hard- and software for recording transients and for setting the wavelength. Experimental measurements of the kinetics of decay of the CH_3 radical in SF_6 bath gas are in the interval $\pm 10\%$ of the literature value. The equipment is intended for measurements of reaction kinetics related to combustion and atmospheric chemistry.

The technique of pulse radiolysis of gases was introduced by Sauer and Dorfman in 1964. A review covering technical aspects and applications to the radiation chemistry of gases has been published.[1] More recently the technique has been used as a tool to study reaction kinetics of free radicals in the gas phase,[2–4] with special focus on systems of interest in atmospheric chemistry and in combustion. For the last 13 years work has been carried out by the Risø group on radical–radical and radical–molecule reactions. One feature of their pulse radiolysis setup is that comparatively high radical concentrations can be obtained, of the order 10^{-6} M. This is an order of magnitude higher than that usually obtained with flash photolysis. A high radical concentration is an advantage in the study of the kinetics, especially for radical–radical combination reactions. The workload on the Risø equipment is high. When a suitable electron accelerator became available it was therefore decided to build another unit for the purpose of investigating radical–radical reactions of relevance in combustion chemistry. The unit is also suitable for laboratory studies of radical reactions occurring in the atmosphere. The equipment was built around a Febetron 708, an accelerator of the field emission type, originally used for pulse radiolysis of liquids and solids.[5,6] The design was adapted from the Risø facility, with modifications caused by the difference between the accelerators used, a 2 MeV Febetron electron accelerator at Risø, and 800 keV equipment with two electron beams used with the Febetron 708. With the

present system the stray-light level is low ($<1\%$), allowing measurements on radicals (e.g. ethyl) absorbing in the UV region.

Equipment overview. The pulse-radiolysis system is built around the Febetron 708, an electron accelerator of the field-emission type. The maximum electron energy is 800 keV. The use of this accelerator for pulse radiolysis of liquids and solids has been described.[5,6] For gas-phase kinetics 600 keV is used. The half-width of the electron pulse is 3 ns and the peak current is 10 kA. The radiation dose can be varied by inserting attenuators with an equal number of holes but with different hole diameters in the electron beam path. To compensate for an inhomogeneous dose the Febetron is equipped with two field-emission tubes in such a way that the gas cell containing the sample gas is irradiated from opposite sides. This creates a relatively homogeneous dose in the sample. The influence of the remaining inhomogeneity has been considered (see below) and has been found to have only minor effects on the measured kinetics.

A schematic overview of the equipment is shown in Fig. 1. The gas samples are irradiated in a 1 L stainless-steel gas cell through thin stainless-steel membranes. The transient optical absorption that occurs in the sample on irradiation is analysed with respect to optical density and time dependence with the aid of the light from a 150 W xenon lamp. To increase the signal-to-noise ratio the luminosity of the lamp is increased by pulsing. The light passes the sample through suprasil quartz windows of the cell at right angles to the electron beams and further

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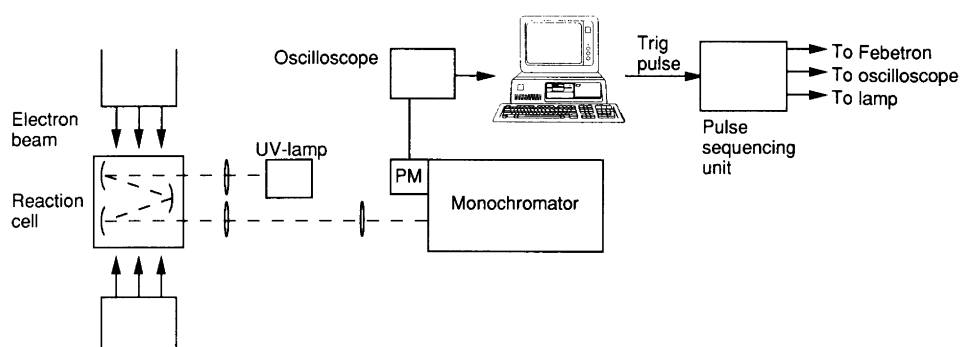* To whom correspondence should be addressed.

Fig. 1. Schematic drawing of the equipment for pulse radiolysis of gases.

through suprasil lenses to a monochromator (McPherson type 2061) coupled to a photomultiplier tube for light detection. The PM tube (R 928) has a short rise time and a high spectral sensitivity from 185 to 930 nm. The output signal is recorded in a digitizer (Tektronix 7912 AD). The Febetron is fired at a preselected time with a pulse sequencing device (Studsvik AB) which also triggers the digitizer and the lamp pulser. Details of the equipment differing from systems described before[1–4] for gas-phase pulse radiolysis are described below.

Sample preparation. The gases are admitted to the evacuated gas cell through a stainless-steel vacuum line. For the evacuation a turbomolecular pump is used to reach a vacuum of ca. 10^{-6} mbar. Gas samples are prepared by introducing the components one at a time and reading the corresponding partial pressure with an absolute manometer (MKS Baratron model 170) with a resolution of 0.1 mbar.

Gas cell. The gas cell, made of stainless steel, is schematically shown in Fig. 2. The optical arrangement in the cell consists of a set of mirrors that allow for multiple passages of the White-type gas cell. It is of a similar design as described elsewhere,[1] except that there are two windows at opposite sides for the electron beams which penetrate through thin stainless-steel foils. The relative radiation dose at each foil is monitored by thermocouples.

Detection equipment. The analysing light of a xenon lamp (Cermax 150W) is pulsed to increase the signal-to-noise ratio in the detection of transient species by UV absorption. A lamp pulser constructed at Risø increases the luminosity 20–50 times for a duration of several milliseconds. The output from the lamp is stabilized with an optical feedback system as described previously.[2]

The White type of mirror system of the gas cell allows for multiple passes of the analyzing light through the sample as indicated in Fig. 2. The experiments are usually carried out using 4, 8 or 12 traversals, corresponding to an optical path length of 40, 80 or 120 cm; respectively. The quality of the aluminium coating of the mirror is essential for light transmission in the UV region. The
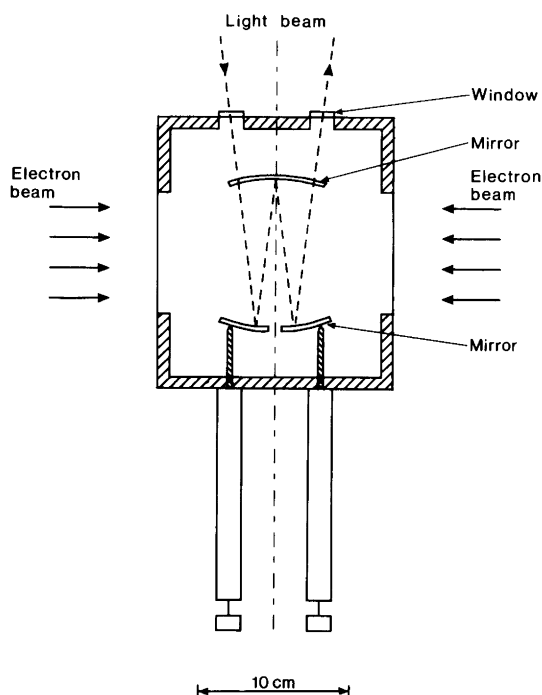

Fig. 2. Gas cell with White-type mirror system.

stray light was measured with suitable cut-off filters. The stray light at 200 and 216 nm was less than 1%. Measurements can be performed at wavelengths down to 205 nm with properly prepared coatings. (We are indebted to the Risø Laboratory and the Applied Physics Laboratory in Linköping for help to prepare the aluminium coatings by vapour deposition).

The monochromator (McPherson type 2061) with a 1200 groove mm^{-1} grating has a reciprocal resolution of 0.8 nm nm^{-1} slit width. The wavelength is set by means of a scan controller (McPherson type 788) driving a stepping motor. The scan controller is interfaced to a PC computer allowing wavelength selection from the keyboard.[7]

The digitising equipment (Tektronix 7912 AD) is controlled by a PC with a specially written software package

for signal retrieval and treatment.[7] A sequence device providing start pulses for the lamp, triggering of the digitizer and the Febetron has been designed. The same unit reads the voltage corresponding to the analysing light intensity I_0 through the gas cell a few microseconds in advance of the firing of the Febetron.

Data-handling system. A PC-based data-handling system has been designed to control the measurements. The measurement sequence is started from the keyboard or manually by a firebutton on the sequencer. The voltages from the thermocouples in front of the electron tubes are amplified ca. 6000 times and digitised in real time with an A/D card (RealTime Devices AD200). The peak signals are stored as measures of the doses. The time-dependent signal from the photomultiplier caught by the digitizer is transferred to the PC. The same data-handling system is used for wavelength selection. The software is written in TBASIC allowing for easy communication between the PC and the attached instruments (digitizer and the wavelength controller). A number of signal treatments can be made by a menu-operated user interface.

A detailed description (in Swedish) is available.[7] The software consists of subprograms for each feature. Replacement of the digitizer, for instance, would require a corresponding change in one subroutine only.

Analysis of absorbance transients

The raw data consist of the transient signal proportional to the light transmittance through the sample. The voltage corresponding to the light intensity before the Febetron is fired is stored in the first few points of the transient. The reduction of the data to absorbances, the subtraction of background signals and the analysis of the data in terms of zero (constant absorption) first- and second-order kinetics is done with software programs developed previously.[6]

The experiments performed so far have been concerned with the recombination kinetics of alkyl radicals and measurements of the combination rate constant between alkyl and hydroxyl radicals. In the former case the analysis is by least-squares fitting. Expressions such as eqn. (1) can be fitted to the data. As many first- and

$$OD(t) = OD(\infty) + \sum_i C_i \exp(-k_i t) + \sum_j C_j/(1 + C_j k_j t) \tag{1}$$

second-order terms as needed can be included. For practical applications the constant absorbance $OD(\infty)$ and at most two first- or second-order terms have been used. The program has been rewritten in QuickBasic, resulting in a much faster analysis. A non-linear least-squares fit with two absorptions decaying simultaneously is completed within seconds rather than in minutes used by the previous program. An example of an absorbance transient for methyl radical recombination kinetics is shown in Fig. 3, together with a second-order fit. The methyl radicals were generated by pulse radiolysis of methane
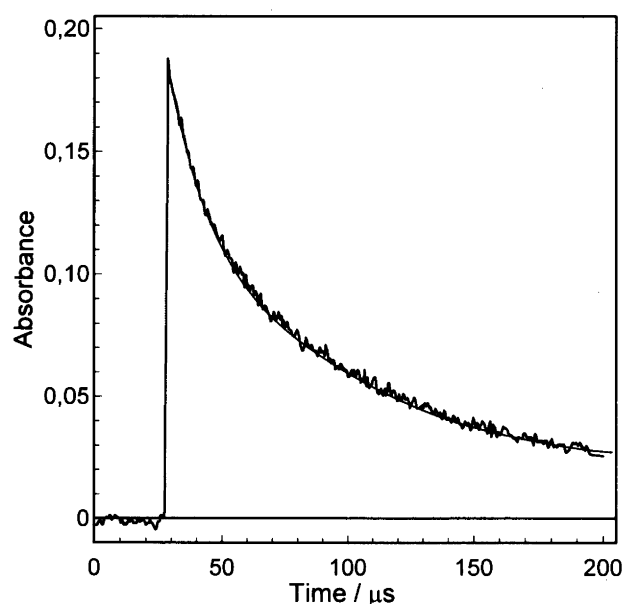

Fig. 3. Absorbance transient of methyl radicals obtained by pulse radiolysis of 3 mbar methane and 50 mbar SF_6 in argon to 1000 mbar. The smooth curve is a fit of the recombination kinetics for $CH_3 + CH_3 \xrightarrow{2k}$ products with $2k = 7.0 \times 10^{10} \, M^{-1} \, s^{-1}$.

and sulfur hexafluoride in an argon atmosphere. The rate constant at room temperature was estimated as $2k = 7.0 \times 10^{10} \, M^{-1} \, s^{-1}$.

Measurements of the hydroxyl kinetics are complicated by the fact that the linewidth is narrower than the resolution of the monochromator, resulting in deviations from the Lambert–Beer law. A correction of the type discussed by Sauer[1] has been implemented in the program. Experience with this correction is as yet limited.

To obtain the combination rate constant between an alkyl radical ($R = CH_3, C_2H_5$) and hydroxyl the following procedure was used. The radicals were generated by pulse radiolysis of alkane–water mixtures in SF_6, see below and Refs. 12 and 13. The effect of reaction (2) on

$$R + OH \xrightarrow{k_{12}} products \tag{2}$$

the overall decay kinetics of the alkyl radicals was studied by varying the concentration ratio of alkane and water. By changing this ratio the relative yields of alkyl and hydroxyl radicals were controlled. The initial alkyl radical decay rate in the presence of hydroxyl radicals can be expressed as eqn. (3), where the subscript 0 indicates the

$$\left(\frac{d \ln[R]}{dt}\right)_0 = -(2k - k_{12})[R]_0 - k_{12}[F]_0 \tag{3}$$

conditions at the end of the electron pulse. $[F]_0$ is the initial concentration of F atoms, which was obtained as described below, and $2k$ is the recombination rate of the alkyl radicals. The assumption was made that $[R]_0 + [OH]_0 = [F]_0$. Code to compute the slope $(d \ln[R]/dt)_0$
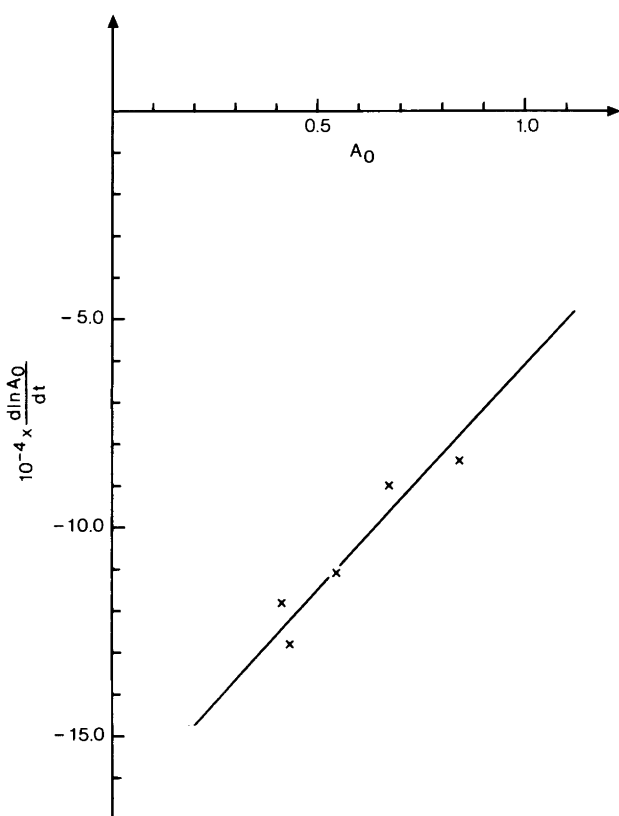
Fig. 4. Initial logarithmic slope of the CH_3 radical concentration as function of the initial CH_3 concentration, A_0 μM, in gas mixtures with varying contents of methane and water in SF_6 to a total pressure of 500 mbar. The initial concentration was measured at $\lambda = 216.4$ nm at a bandwidth of 0.4 nm with $\varepsilon(CH_3) = 10\ 800$ M^{-1} at room temperature. The intercept on the y-axis gives a value $k_{12} = 1.0 \times 10^{11}$ M^{-1} s^{-1} for the $CH_3 + OH$ combination rate.

and the concentration $[R]_0$ from the absorbance transients has been incorporated in the program. k_{12} may then be calculated both from the slope and the intercept, if k and $[F]_0$ are given. The data for $R = CH_3$ are shown in Fig. 4. The combination rate constant with SF_6 bath gas at 500 mbar is estimated as $k_{12} = 1 \times 10^{11}$ M^{-1} s^{-1}. To refine the estimate so obtained simulations with the program CHEMSIMUL, now available in a PC version. are used.[8] The rate and concentration parameters are adjusted to obtain a good fit of the simulated transient concentration curve to the experimental data. For the above-mentioned system $k_{12} = 7.3 \times 10^{10}$ M^{-1} s^{-1} was obtained.

Dosimetry

Absolute dosimetry is not essential for the application to radical kinetics. A relative measure of the dose at each experiment, the radical concentration obtained in each shot, and the dose distribution in the gas cell are necessary to obtain correct kinetics. The relative dosimetry by means of thermocouples is described

above. Concentration measurements, dose distribution measurements, and the influence of an inhomogeneous distribution on the kinetics are described below.

Radical concentrations

A wide range of free radicals can be produced by the H-atom abstraction of F atoms[3,4] obtained from the radiolysis of sulfur hexafluoride, reactions (4) and (5).

$$SF_6 \rightarrow F + products \tag{4}$$

$$F + RH \rightarrow HF + R \tag{5}$$
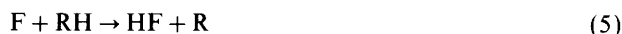
The concentration of methyl radicals produced in reaction (5) has been measured at room temperature at 216.4 nm with a bandwidth of 0.4 nm using the recommended value of $\varepsilon(CH_3) = 10\ 800$ M^{-1} cm^{-1}.[9] At CH_4 concentrations higher than about 2 mbar all F atoms produced by pulse radiolysis of 1000 mbar SF_6 are converted quantitatively into methyl. This gave a concentration of $[F]_0 = 2.4$ μM, with an uncertainty of $\pm 10\%$ depending on variations of the dose. As seen from Fig. 5 the F-atom concentration increases linearly with increasing SF_6 pressure.

A quantitative measure of the dose was made by irradiating pure oxygen gas. Using a G-value of 12.8,[10] the dose was calculated from eqn. (6), where $[O_3]$ is in μM

$$D(Gy) = 0.75[O_3]/\rho \tag{6}$$

and ρ is the density of the gas in kg dm^{-3}.

A concentration of $[O_3] = 0.52$ μM was measured at 1000 mbar O_2 when irradiating through steel membranes
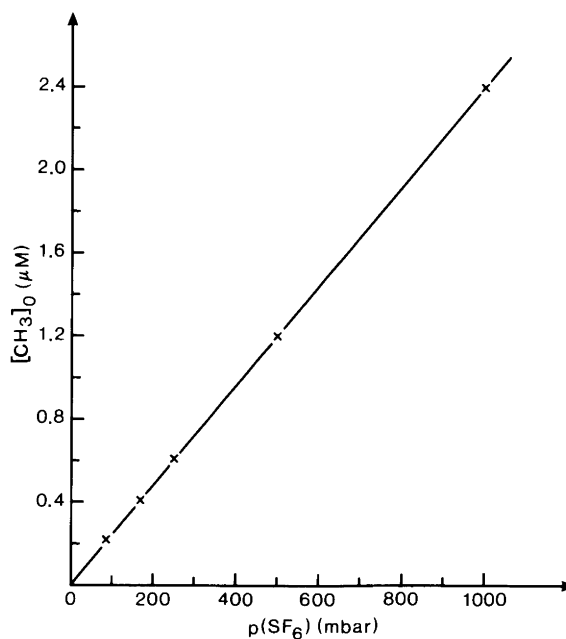

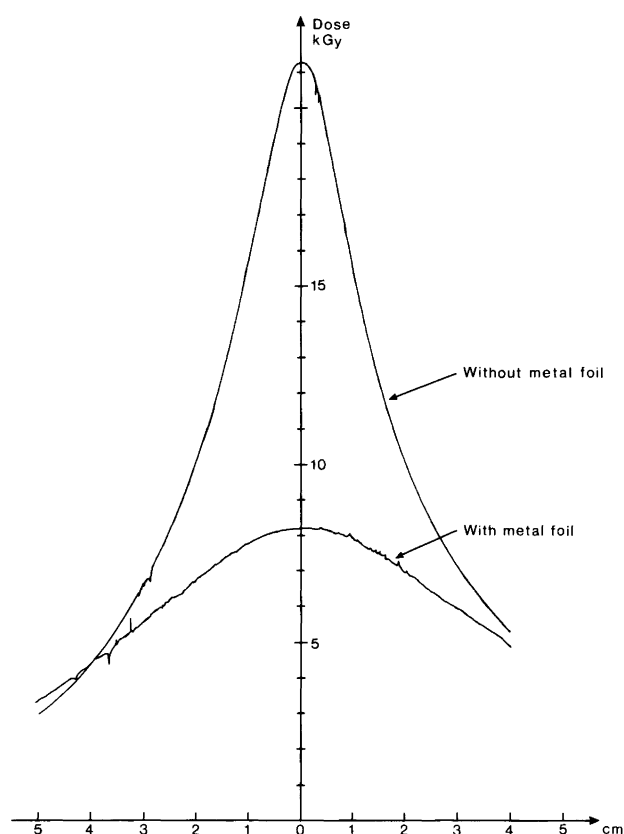*Fig. 5.* Effect of SF_6 gas pressure on the yield of CH_3 radicals from methane.

Fig. 6. Dose distribution measured with radiochromic dye film along the direction of the analysing light (a) with radiation windows of 0.06 mm stainless steel and (b) without radiation windows. The film was exposed to 10 electron pulses. The dose distribution is almost symmetrical about $x = 0$. The mirrors are at $x_0 = \pm 5$ cm, but the dose was measured out to $+4$ cm only.

of 0.06 mm thickness of the gas cell. The measured dose of 275 Gy is an average along the path of the analysing light beam. The dose in other gases may be calculated from relative stopping powers. The steel membranes reduce the radiation dose in the centre of the cell by a considerable amount. The steel membranes also make the dose distribution more homogeneous, cf. the doses measured in the direction of the analysing light with and without the steel membranes (Fig. 6). This is a considerable advantage for kinetics measurements. The remaining inhomogeneity and its effect on second-order kinetics are considered in the next section.

Dose distribution: effect on kinetics

The dose distribution along the path of the analysing light of the gas cell has been measured using radiochromic dye film strips. The dose distribution between the centres of the mirrors in the plane perpendicular to the electron beam is shown in Fig. 6. The separation between the mirrors is 10 cm. As can be seen from the figure the dose drops to ca. one half at the mirrors in comparison with the

centre of the cell. The dose measured along the electron beam was not significantly different at the edges and at the centre of the light path, determined by the width of the mirrors. The dose distribution perpendicular to the analysing light and the electron beam is nearly the same as along the light path. The dose variation over the distance defined by the width of the mirrors is ca. 5%, much less than the variation along the analysing light.

The effect of the dose inhomogeneity on second-order kinetic data has been considered by Boag,[11] Sauer[1] and more recently by Ellermann.[4] In all treatments the initial radical concentration was taken proportional to the experimentally determined dose distribution along the path of the analysing light.

In the treatments of Boag and Sauer an analytical expression was used for the dose distribution along the analysing light path.[1,11] A similar analysis of the present equipment gave the following results. The dose distribution in Fig. 6 is assumed to give rise to a concentration distribution of the form of eqn. (7a) or (7b). x is the distance from the centre of the cell along the light path.

$$c_0(x) = A - Bx^2 \tag{7a}$$

$$c_0(x) = A/(1 + Bx^2) \tag{7b}$$

The mirrors are at $x_0 = \pm 5$ cm from the centre. The former equation applies to the conditions at normal operation with the dose distribution shown in Fig. 6a, the latter to the distribution shown in Fig. 6b.

The measured concentration for a second-order reaction with rate constant k is given by eqn. (8).[1,10] Performing the integration using eqn. (7a) gives eqn. (9), with I_1, a and b given by eqns. (10), (11) and (12), respectively.

$$c_{\text{mean}}(t) = \frac{1}{2x_0} \int_{-x_0}^{x_0} \frac{c_0(x)}{1 + c_0(x) \cdot 2kt} \, dx \tag{8}$$

$$c_{\text{mean}}(t) = \frac{1}{2kt}\left(1 - \frac{I_1}{2x_0}\right) \tag{9}$$

$$I_1 = \frac{1}{(ab)^{1/2}} \log \frac{a + x_0(ab)^{1/2}}{a - x_0(ab)^{1/2}} \tag{10}$$

$$a = 1 + 2Akt \tag{11}$$

$$b = 2Bkt \tag{12}$$

Simulations based on eqn. (9) have been made for $CH_3 + CH_3$ recombination kinetics. A concentration of $c_{\text{mean}}(0) = 1.1 \, \mu M$ was taken from experimental data using the extinction coefficient $\varepsilon(CH_3) = 10\ 800 \, M^{-1}$ cm^{-1} for the absorption at 216.4 nm. From eqn. (9) one has $c_{\text{mean}}(0) = A - Bx_0^2/3$. A least-squares fit of eqn. (7a) to the dose profile in Fig. 6 then gave $A = 1.40 \, \mu M$ and $B = 0.0354 \, \mu M \, cm^{-2}$. A rate constant of $k = 3.5 \times 10^{10} \, M^{-1} \, s^{-1}$ was used to simulate a transient with eqn. (9).

The transient was then analysed by a least-squares fit of a pure second-order kinetics curve. It was found that the fitting so obtained was very close to that from eqn. (13).

$$c_{mean}(t) = \frac{c_{mean}(0)}{1 + 2c_{mean}(0)\,kt} \qquad (13)$$

The rate constant measured over the first half-life is 3 % too large, and the deviation becomes less, 1–2 % at longer times. According to this analysis the rate constant is not seriously affected by an inhomogeneity of the radiation dose of the symmetry and magnitude shown in Fig. 6. Larger deviations would have resulted for the dose distribution obtained without radiation windows. This dose distribution and the corresponding concentration distribution in eqn. (7b) would give rate constants that are too large by 4–8 %. Another unfavourable condition is when the distribution becomes unsymmetric. This was the case in the measurements reported by Sauer.[1] An exponential decay of the dose rate parallel to the analysing light was observed. An analysis analogous to that described above gives a rate constant for the methyl kinetics that is too large by ca. 15 %. For this reason the relative doses of the two tubes are always monitored.

Experimental measurements of the kinetics of the decay of the CH_3 radical in SF_6 bath gas at 1000 mbar and 293 K have been made to check the reproducibility of the system. 83 % of the data from 30 measurements are in the interval $\pm 10\%$ of the 'recommended' literature value, $k = 3.5 \times 10^{10}\ M^{-1}\,s^{-1}$.[9]

Conclusions

The equipment described above for pulse radiolysis of gases allows measurements of radical reaction kinetics in the time interval 1×10^{-8}–5×10^{-3} s. The upper limit is set by the maximum time for lamp pulsing. As yet it has not been of interest to reach the lower limit, set by the pulse length and the rise time of the detection system. Owing to the low electron energy the equipment can be operated with small arrangements for radiation protection. The photoelectric detector is placed in the same room as the accelerator, allowing for a compact optical system. The stray light level is low, down to 200 nm, allowing detection of, for instance, alkyl radicals which absorb in the UV wavelength region. The upper wave length limit of ca. 900 nm is set by the sensitivity curve of the photomultiplier.

Hard- and software permit registration of kinetic transients in digital form, together with parameters such as the relative radiation dose, the intensity of the analysing light and comments defining the conditions of the experiments. The resulting data are stored on disks readable by personal computers. The equipment has been used to measure the combination kinetics of CH_3 and C_2H_5 radicals with OH at room temperature.[12,13]

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