

Study of the Spectra and Recombination Kinetics of Alkyl Radicals by Molecular Modulation Spectrometry

Part 1.—The Spectrometer and a Study of Methyl Recombination between 250 and 450 K and Perdeutero Methyl Recombination at Room Temperature

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Using the technique of molecular modulation spectrometry, the rate constant for methyl radical recombination has been measured to be $(4.0 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ between 250 and 450 K. The rate constant for perdeuteromethyl radicals is identical (within 20 %) at room temperature. With 0.6 nm resolution the effective peak absorption cross-section for methyl radicals at 216 nm is $(3.2 \pm 0.6) \times 10^{-17} \text{ cm}^2$, consistent with an absolute cross-section of $(4.2 \pm 0.8) \times 10^{-17} \text{ cm}^2$. With a resolution of 1.0 nm the observed maximum cross-section for CD_3 absorption, 3.0×10^{-17} , is consistent with an absolute cross-section of $(1.0 \pm 0.2) \times 10^{-16} \text{ cm}^2$.

Alkyl radical recombination reactions are important because of the part they play in the pyrolysis of hydrocarbons.¹ They are also the reference reactions against which many other reactions have been compared and their rate constants deduced from product analyses of reacting mixtures.² There are, furthermore, theoretical problems in reconciling measurements of the rate constant for alkane dissociation and its pressure dependence with measurements of recombination.^{3, 4} For all these reasons, the dissociation of alkanes and the recombination of alkyl radicals have been studied extensively over the past 30 years, but whilst there was a reasonable unanimity about the rates of the reactions until a few years ago, there has been considerable dispute recently. This has arisen because new techniques,⁵ in particular the radical-buffer method of Benson and his co-workers and the very low pressure pyrolysis method developed by Golden and his colleagues, have given results different from the previously accepted values. These new techniques do not make measurements of the free radical kinetics by monitoring the radicals *in situ*, but rely upon the interpretation of sampled product analyses albeit from novel experiments. In the light of this work much of the earlier pyrolysis is being reinterpreted using lower rate constants for alkyl combination.⁵ It is important to obtain unequivocal measurements on these reactions and the method of molecular modulation spectrometry devised by Johnston *et al.*⁶ offers the opportunity of observing the radicals themselves, if their absorption spectra are known or can be discovered. We have built such a spectrometer to operate in the ultraviolet and have used it to study the following alkyl radicals: methyl, perdeuteromethyl, ethyl, isopropyl and t-butyl. In this paper we describe the apparatus and the interpretation of our results, illustrating the method by the data obtained on methyl and perdeuteromethyl reactions. The rate constants here are subject to much less dispute; the other alkyl radicals are discussed in the following paper.⁵

There are four recent flash-photolysis experiments, three with spectroscopic monitoring at 216 nm⁷⁻⁹ and one mass-spectrometric,¹⁰ which give a rate constant

for methyl recombination at room temperature close to the earlier rotating sector values: $k = (4 \pm 1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($10^{13.4} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). One high intensity flash-photolysis experiment with spectroscopic monitoring at 154 nm,¹¹ leads to a result twice the accepted value, but because chemical analysis showed that products other than ethane were formed, this result looks less reliable. Apart from a shock-tube measurement,¹² there is little information on the temperature dependence. We have reported a preliminary result close to the accepted value¹³ and here give the results of a more complete analysis of more extensive data at room temperature, and also results over the range from 250 to 450 K.

There appears to be only one measurement of the rate of combination of perdeutero methyl radicals, *i.e.*, an early rotating sector result¹⁴ that was identical to the methyl rate in an identical apparatus. More recently^{15, 16} two reports have appeared of large isotope effects (factors of 6 to 10) in the half-pressure in the fall-off region. A significant isotope effect in the high-pressure rate constant has also been predicted theoretically.¹⁷ This study has been restricted to high pressures at room temperature.

EXPERIMENTAL

There has been an upsurge in interest in using modulation techniques to measure both weak emissions and absorptions. The principles behind the "molecular modulation spectrometry" technique have been described by Johnston and his co-workers,^{6, 18} The latter citation¹⁸ also gives the mathematical basis of their analysis of the experimental data. The apparatus we have constructed differs in several important respects from theirs and is described in detail in the following section.

APPARATUS

A schematic diagram of the system is given in fig. 1. The reaction vessel used at room temperature is a quartz cylinder 60 cm long and 4 cm in diameter connected to a conventional glass vacuum system and pumped by an oil diffusion and 2-stage rotary pump. Teflon stopcocks are used in the experimental sections. The vessel used over a range of temperature is 2 cm in diameter and is surrounded by a concentric double walled pyrex vacuum vessel;

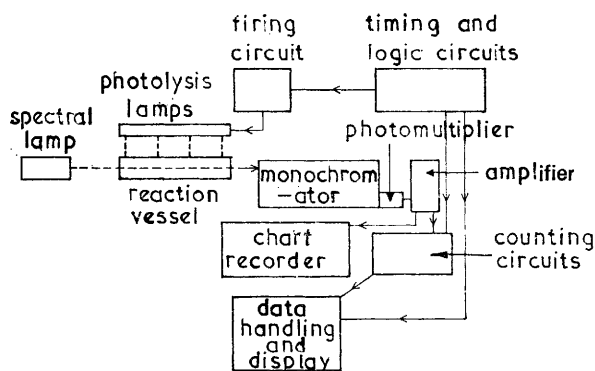


FIG. 1.—Block diagram of apparatus.

each end of the cell has a double window with a vacuum space in between. Either hot air or cooled N₂ is blown through the space between the cell and the vacuum jacket, and the temperature in the cell is monitored by four thermocouples attached to the cell wall. Temperatures between 240 and 450 K can be reached. At 373 K the temperature of all the couples is within 4 K and at 450 within 10 K. In both series of experiments the cell is filled with a static mixture of gases made up either directly in the cell (when the components are left for

24 h to mix) or from a magnetically stirred mixing vessel. Low pressures (up to 10 Torr) are measured with a Furness transducer (MDC Micromanometer) calibrated against a silicone oil manometer and higher pressures (up to 760 Torr) with an S.E. Labs transducer (SE1150) calibrated against a mercury manometer.

The reaction vessel (or vessel and pyrex jacket) is surrounded by six 20 W, 2 ft long Philips "Dark-Light" fluorescent tubes (TL20W/08) with the whole assembly in a reflecting aluminium can. The tubes are weakly pre-ionized by an R/F oscillator housed on the side of the can and can be switched on and off at any frequency between 10^2 and 10^{-2} Hz by a power transistor controlled by a suitable square wave.¹⁹ Alternatively, 18 in long 15 W low pressure mercury lamps (Phillips TUV15) may be substituted. These lamps are not made in 2 ft lengths and consequently the photolysis is less uniform; they have been used for the semi-quantitative work in generating alternative radical sources, with quantitative results taken using the "dark lights". As the low pressure lamps polarize they cannot be used at frequencies below 1 Hz. The "dark lights" emit between 300 and 400 nm with the peak emission near 355 nm, and the low pressure lamps at 254 nm. Their flashing produces a modulated number of free radicals in the reaction cell when it contains a suitable photo-dissociating substrate.

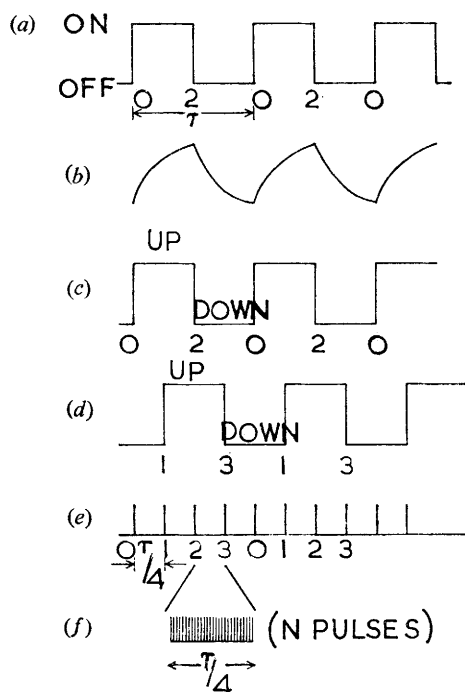


FIG. 2.—Timing relationships in molecular modulation spectrometer. (a) Photolysis lamp output, (b) radical concentration and absorption, (c) in-phase up/down counting, (d) in quadrature up/down counting, (e) modulo- n counter output with coding, (f) input to modulo- n from crystal oscillator.

Radicals are detected by measuring the modulated component produced by their absorption in the light from a monitoring lamp shining along the axis of the cell. The lamp is a 40 W deuterium lamp with a spectro-sil window (Manufacturers' Supply Co.) and to prevent spurious signals arising from changes in the monitoring intensity both the voltage across and the current through the lamp are stabilized by operational amplifier feedback circuits. The light output contains no periodic components greater than 1 part in 10^6 that bear a fixed phase relationship to the photolysis lamp switching frequency. In contrast to Johnston's

experiments, where the monitoring light is chopped at a relatively high frequency, the monitoring signal is unmodulated and the signal is detected by a very low frequency amplifier and detection circuit. This halves the experimental time to reach the same signal-to-noise ratio, other factors being equal. After passing through a double 0.33 m monochromator (Rank Precision Industries D330/1) the monitoring beam is detected by a blue-sensitive photomultiplier (EMI 9665B). The dispersion of the instrument is 1.2 nm mm^{-1} giving a resolution of 0.6 nm at the slit width of 0.5 mm used in most of the kinetic work.

The alternating component (a.c.) in the photomultiplier output is amplified and the d.c. level (which is monitored) is subtracted out. To achieve this, the output from the photomultiplier is sampled through a metal oxide semiconductor field effect transistor (M.O.S.F.E.T.) gated once per photolysis cycle just prior to lamp switch-on, and this sample voltage is held on one input to a very low input current operational amplifier (Analog Devices 311 K). The other input takes the continuous photomultiplier signal and the output is the varying signal without the d.c. level. With care taken about the cleanliness of the operational amplifier mounting to reduce leakage currents, the circuit will pass 10^{-2} Hz pulses without significant droop. The signal from the subtracting amplifier together with an adjustable d.c. voltage is amplified between 10 and 100 times in a second operational amplifier and then fed to a voltage-to-frequency converter (Ancom VFC 15VF-1); the d.c. voltage serves to adjust the output here to the d.c. level necessary for the next stage and is in itself arbitrary.

The measurement of the a.c. is performed by the voltage-to-frequency conversion followed by up-down counting. The timing relationships in the detecting circuit are given in fig. 2, where it can be seen that both the lamp-firing and measuring circuits are timed from the same 7.2 MHz master crystal oscillator. The v.f.c. gives high frequency (MHz) pulses at a rate proportional to the input voltage and these pulses are then counted by a pair of up-down counters,²⁰ one "in-phase" which counts up when the lights are on and down when they are off and the other, "in-quadrature", switches from down to up midway through the "on" period and *vice versa* midway through the off. As a result, any signal with a component in phase with the light gives a steadily increasing count in the in-phase channel whilst random noise signals are averaged out; an in-quadrature component accumulates similarly in the corresponding channel. The resulting counts are displayed digitally together with the experimental time and the number of cycles over which they have been accumulated. The sensitivity of the system is calibrated by feeding an "in-phase" square wave of known size into one of the inputs of the differencing amplifier. This same square wave can also be used, if necessary, to cancel out scattered light from the photolysis lamps by adding it to the photomultiplier output to bring the in-phase signal to zero at high frequency where any genuine absorption would be in-quadrature. The total counting period may be preset to a chosen value, typically to 100 s, in which time the signal-to-noise ratio approaches 1 for an absorption of 3×10^{-5} at frequencies above 1 Hz. At lower frequencies the residual excursions arising from noise are larger in a given period.

The timing period is set by adjustable modulo- n counters, integrated circuits which give out one pulse at every n th successive input, with n being set to give pulses at a frequency four times that of the inverse of the chosen period. These pulses are coded in successive groups of four with each pulse in the group coded to switch the appropriate counter and lamp once per cycle, as shown in fig. 2. With the current experimental programme, where the absorptions are strong and easily measurable in 100 s or so, the apparatus is manually controlled, but it is designed to be run by a programmable calculator which could control a search for a weak signal requiring much longer integration times.

EXPERIMENTAL METHOD

The experimental procedure is to fill the cell and then to search for an absorption by working with a fixed photolysis period and number of photolysis lamps and varying the wavelength. Alternatively, with a radical whose absorption spectrum is known, the monochromator is set to an appropriate wavelength and the absorption is measured at different photolytic periods and with differing numbers of photolytic lamps. The rate of consump-

tion of substrate is measured from the decline in signal with total photolysis (no. of lamps \times time). The rate of photolysis is then calculable throughout an experiment (*q.v.*). The emission from "dark lights" of equal age is very similar and the intensity of photolysis is varied independent of substrate pressure by varying the number of lamps.

The build-up of products on photolysis has been followed gas chromatographically in separate experiments. Gas samples of 1 cm³ were drawn from a reaction vessel similar to that used in the spectrometric work through a "Suba-seal" on a side arm using a gas syringe (Hamilton) with a 6 in long needle. Samples were taken from time to time during a photolysis and analysed on a 50 ft \times 0.020 in i.d. stainless steel column coated with Ucon LB 550X (Perkin-Elmer) at 40°C, with flame ionization detection. Retention times and calibrations were obtained by sampling known mixtures from the reaction vessel by the same method. The good correlation between the relative molar sensitivities towards, for example, hexamethylethane and isobutane, 0.48 to 1.00, and that expected from the general rule of equal weight sensitivity per g carbon for hydrocarbons, 0.50 : 1.0, suggests that we are not having any problems with the method, even for the former low vapour pressure hydrocarbon. Here the reaction vessel was again surrounded by six "dark lights" in a similar geometry to that used with the molecular modulation spectrometer. The lamps were run on a.c. with the conventional ballast circuitry and switched on and off manually. The rate of photolysis was measured by monitoring t-BuO₂ radicals directly by absorption, earlier work²¹ having shown that the photolysis rate measured from observations of peroxy radicals was identical to that of the corresponding alkyl radical. The relative photolysis rates of different azo compounds in the same situation are known from the molecular modulation studies. In this way chromatographic yields could be compared with those predicted from the rate of photolysis.

The azomethane was prepared by the standard method²² with the perdeutero compound preparation based on the same scheme.^{22, 23} Infrared and mass spectrometric analyses showed that their purities were better than 99 % and the gas chromatographic analysis during photolysis showed that the impurity levels remained unchanged. The isotopic analysis of the perdeutero compound was: C₂D₆N₂, 80 %; C₂D₅HN₂, 10 %; C₂D₄H₂N₂, C₂D₃H₃N₂, C₂D₂H₄N₂ all 3 %. White-spot nitrogen and oxygen from B.O.C. were used as supplied.

ANALYSIS OF RESULTS

In their infrared and ultraviolet spectroscopic studies,⁶ Johnston *et al.* used lock-in amplifiers to detect the modulated absorption signals. The output from their equipment came therefore as a signal amplitude, *A*, and a phase relationship, ϕ , between the signal and the photolysis light. From the variation in *A* and ϕ with flashing frequency and a model of the experimental chemistry, they deduced the rates of the chemical reactions they were studying. With the method of measurement used here, the results appear in a different form: separate in-phase and in-quadrature absorptions are measured at each frequency. We use, as a result, a different method of handling our data. It is similar to that outlined by Wu and Johnston²⁴ in describing an apparatus with mass spectrometric detection.

It can be seen from fig. 2, by comparing the counting periods shown in (c) and (d), with the signal *a(t)* shown in (b), that the in-phase counting rate, *R*, is given by

$$R = \frac{F}{\tau} \left[\int_0^{\tau/2} a(t) dt - \int_{\tau/2}^{\tau} a(t) dt \right] \quad (1)$$

and the in-quadrature counting rate *Q* is given by

$$Q = \frac{F}{\tau} \left[\int_{\tau/4}^{3\tau/4} a(t) dt - \int_{3\tau/4}^{5\tau/4} a(t) dt \right]. \quad (2)$$

F is the calibration factor relating count rate and absorption. There is an initial period after the start of an experiment when *R* and *Q* change as the steady level,

about which the radical density oscillates, is reached. In our computer simulations we start at switch-on and calculate until R and Q reach these constant values. In the experiments we allow sufficient time after switch-on or changing frequency to reach steady conditions before taking a reading. The form of the experimental results can be calculated analytically for simple chemical models and the results of

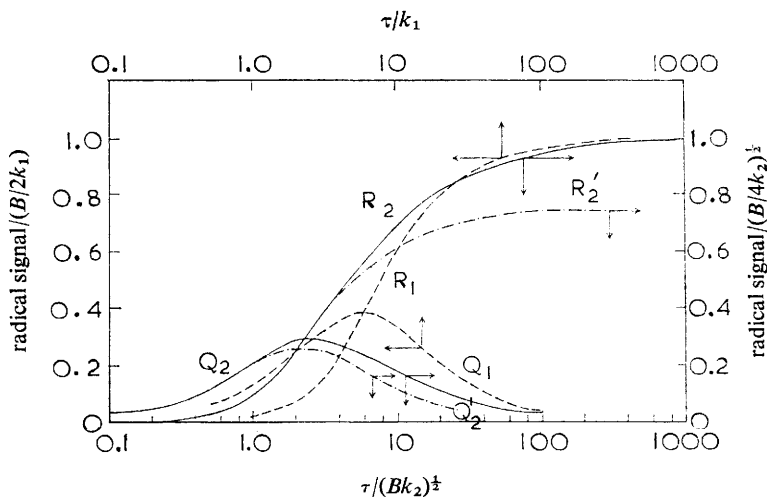


FIG. 3.—Radical signals in molecular modulation spectrometry: (a) ---, first order; (b) —, second order; (c) —·—, second order+first order $k_1/4(Bk_2)^{1/2} = 0.3$.

such calculations are shown in fig. 3. Curve (a) gives the results for first-order kinetics:

$$dn/dt = B - k_1 n, \text{ where the lights are on} \quad (3)$$

and

$$dn/dt = -k_1 n \text{ in the dark.} \quad (4)$$

n is the radical density, B is the photolytic rate of radical production and k_1 is the rate constant at which radicals disappear by first-order kinetics. Curve (b) gives the results for second-order radical removal:

$$dn/dt = 2B - 2k_2 n \text{ in the light} \quad (5)$$

and

$$dn/dt = -2k_2 n \text{ in the dark.} \quad (6)$$

k_2 is the rate constant of the reaction (6) defined as the rate of product formation. Radicals are removed at twice this rate and similarly two radicals are produced in the photolytic act. The form of the results is similar in both cases. At relatively low frequency the radicals keep up with the light and their density follows a similar square wave against time. The in-phase count rates approach limiting values given by half the steady-state solutions of eqn (3) and (5) and the in-quadrature signals approach zero. As the frequency increases, the time constant of the reactions become significant, the in-phase signals fall and those in-quadrature rise. The curves cross where the in-quadrature signals reach their maximum value. At the highest frequencies, the radical density becomes a sawtooth and both signals fall, the in-phase more quickly.

With first-order kinetics, the limiting low frequency absorption, A_0 , and the period at which the curves cross, τ_0 , are given by

$$A_0 = B\sigma l/2k_1 \quad (7)$$

$$\tau_0^{-1} = 1/6k_1 \quad (8)$$

where σ is the radical absorption cross-section and l the path length. Absorptions, A , are always less than 3×10^{-3} and so the transmitted intensity, $I_0 e^{-A}$, can always be taken to be equal to $I_0(1-A)$ where I_0 is the incident monitoring intensity. With first-order kinetics k_1 is given directly by τ_0 and if B is known the absorption cross-section may be obtained from A_0 .

For second-order kinetics

$$A_0 = \frac{1}{2}\sigma l(B/k_2)^{\frac{1}{2}} \quad (9)$$

and

$$\tau_0^{-1} = (Bk_2)^{\frac{1}{2}}/2.2. \quad (10)$$

To measure k_2 it is necessary to know B . In this series of experiments B is measured by following the decline in radical absorption with overall experimental time, *i.e.*

$$B = -\frac{d[X]}{dt} = \gamma I[X] \quad (11)$$

where I is the intensity of the photolysis lamps (proportional to the number), $[X]$ is the concentration of substrate and γ is a composite geometric and absorption factor relating the light intensity and the rate of photolytic decomposition. Providing the substrate is not attacked by radicals, after a period T of photolysis

$$[X] = [X_0] \exp(-\gamma T/2) \quad (12)$$

and the limiting count rate at low speed, ($R_0 = FA_0$)

$$R_0 = \frac{1}{2}F\sigma l[\gamma I(X_0)/k_2]^{\frac{1}{2}} \exp[-\gamma T/4]. \quad (13)$$

B is measured ideally by plotting $\ln R_0$ against T ; fig. 5(a) shows an experimental plot which, although it is slightly curved, is indistinguishable from a straight line. It can be seen from fig. 3, however, that only for very long photolysis periods does R

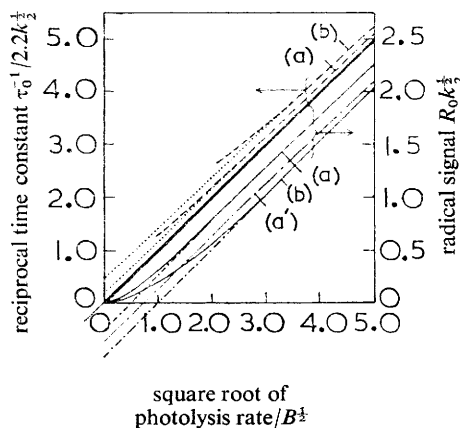


FIG. 4.—Effect of a first-order process added to second order removal on R_0 and τ_0^{-1} : heavy solid line, R_0 and τ_0^{-1} , second order alone, $k_1=0$; (a) $k_1/k_2^{1/2}=2$, —, R_0 ---, τ_0^{-1} ; (b) $k_1/k_2^{1/2}=4$, —, R_0 , ---, τ_0^{-1} ; (a') effect of a finite counting period upon (a) $\tau = 4.0 \tau_0$ at $B^{1/2} = 5$.

approach R_0 . In practice, it is convenient to use a period of $1\text{ s} = 20\text{ to }40 (Bk_2)^{-\frac{1}{2}}$ for alkyl radicals in the present experiments where τ_0 is typically between 0.05 and 0.02 s. On continued photolysis, the substrate is consumed, and the ratio between 1 s and $(Bk_2)^{-\frac{1}{2}}$ falls; the measured R at 1 s falls more rapidly than the count rate at infinite period, and the experimental measurement of B obtained from the slope of the best straight line drawn through the measured values of R_0 needs to be corrected. If t_0 is initially 0.02 s the correction is 12 %; 0.05 s, 26 %.

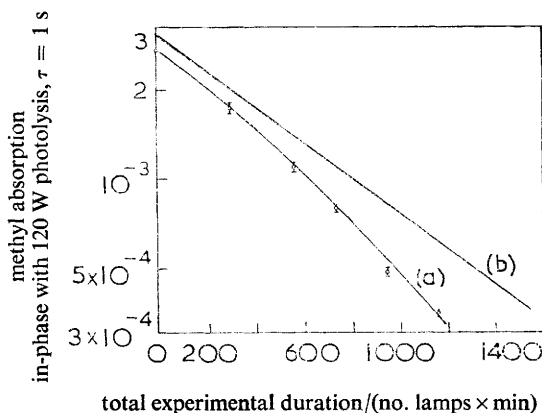


FIG. 5.—Decline in methyl radical absorption with total experimental duration: (a), Φ , experimental points; (b) correction for finite duration of counting period.

Another important simple model to consider is the one in which radicals are lost simultaneously by both first- and second-order kinetics.

$$\text{Lights on: } \frac{dn}{dt} = 2B - k_1n - 2k_2n^2$$

$$\text{Lights off: } \frac{dn}{dt} = -k_1n - 2k_2n^2.$$

An example of the computed effect of a fraction of first-order loss on a system dominated by second-order kinetics is shown in fig. 4. Calculation of the effect upon R_0 is straightforward:

$$R_0 = [B/k_2]^{\frac{1}{2}}[(1 + k_1^2/16Bk_2)^{\frac{1}{2}} - k_1/4(Bk_2)^{\frac{1}{2}}] \quad (14)$$

$$= [B/k_2]^{\frac{1}{2}}[1 - k_1/4(k_2B)^{\frac{1}{2}}]. \quad (15)$$

When k_1 is small, $k_1 < (16Bk_2)^{\frac{1}{2}}$, the straight line plot of R_0 as a function of the square root of the photolysis rate is displaced to give a negative intercept, as shown in fig. 4. The effect upon τ_0 cannot be found analytically but is taken from the computed curves. These show that the in-phase signal is significantly affected at low frequency and is virtually unaffected at high frequency; the in-quadrature maximum is reduced in magnitude and crosses the in-phase curve at higher frequency but the resultant effect upon τ_0 is relatively less than that upon R_0 , as the comparison in fig. 4 shows. For small k_1 , a plot of τ^{-1} against $B^{\frac{1}{2}}$ is a straight line with a positive intercept.

The other basic relationship used in this work is the effect of a change in the reference voltage upon the observed modulated absorptions. Such a change arises from the consumption of the substrate by photolysis, or the formation of an absorbing product. If the substrate is being removed then the transmission increases linearly when there is photolysis and is constant when the lights are off. Given that the

average rate of change with time (over a whole cycle) is ΔV , this results in apparent absorptions of

$$\text{in-phase, } -\Delta V\tau/4; \text{ in-quadrature } +\Delta V\tau/8. \quad (16)$$

Product and reactant absorptions become important at low speed, but experimental parameters are chosen as far as possible to make corrections to transient absorptions small.

RESULTS

METHYL RECOMBINATION AT ROOM TEMPERATURE

The absorption spectrum obtained on the photolysis of azomethane in the presence of a high pressure of nitrogen is shown in fig. 6; the signal from the methyl radical

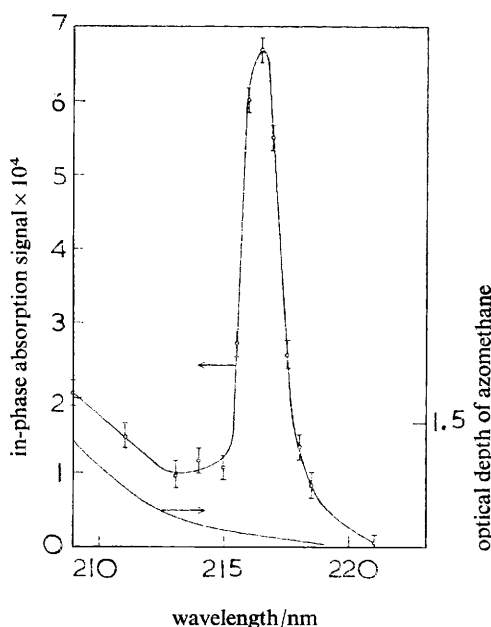


FIG. 6.—Absorption spectrum of methyl radicals: 3.5 Torr azomethane, 315 Torr N_2 , $\tau = 1$ s, photolysis rate = $6 \times 10^{-5} \text{ s}^{-1}$, slit width 0.5 mm.

is seen clearly, but whereas there is no significant “absorption” on the long wavelength side of the band there is an apparent signal to the short wavelength side. The optical depth of the substrate, azomethane, is also shown and the short wavelength signal rises in a parallel fashion. Part of the signals can be accounted for by the consumption of the substrate, but even after this has been corrected for, there remains a residual apparent absorption. At 209 nm, where this signal is of the order of 2×10^{-4} , the optical depth of the azomethane is close to 1.5. The appearance of apparent transient absorptions on the edges of substrate absorption bands has been found in all the systems we have studied. They show up, for example, in $Cl_2 + N_2$ mixtures, a system where there is no overall chemical change, between 270 and 300 nm on the edge of the Cl_2 absorption. The reason for these spurious signals is not fully understood but we suggest that they arise from transient deflections or attenuations of the monitoring beam by the gas convecting, forced by the photolytic heating from the lamps. There must be either small gradients in refractive index arising from small

temperature changes or small changes in substrate density due to some inhomogeneity in photolysis. Whatever the reason, these signals often set the lower limit to the size of signal that can be detected and also the limit to the accuracy with which a rate constant can be measured. Before a new spectrum is confirmed, it is important that it can be produced from substrates which have different absorption characteristics as well as different chemical properties.

Radical kinetics are obtained by fitting full curves of absorption in-phase and in-quadrature as a function of photolysis period. Fig. 7 shows such a plot for one set of

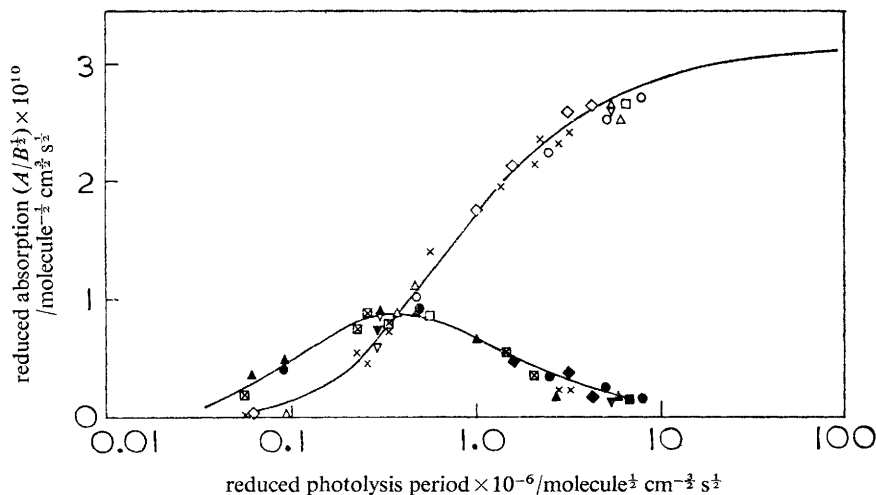


FIG. 7.—The variation in methyl radical reduced absorption with reduced photolysis period. Initial azomethane pressure = 2.85 Torr, N_2 = 150 Torr: Open points, in-phase; filled, in-quadrature; \circ , 6 lamps; \square , 5; \triangle , 4; ∇ , 3; \diamond , 2; \times , 1. Lines drawn for $k_2 = 4 \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$.

methyl radical results; to obtain a plot on which results at all photolytic intensities can be shown, reduced absorption (divided by photolysis rate¹) and times (multiplied by photolysis rate¹) are plotted. All the results are described very well by a pure second-order pair of curves, with the rate constant for methyl combination $k = (4.0 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The concomitant absorption cross-section is $3.2 \times 10^{-17} \text{ cm}^{-2}$. The error is the standard deviation in the different k values needed to fit 10 sets of data. This error is greater than the precision with which any one set of results can be fitted and arises partially from the relatively simple methods used to make up mixtures. In a preliminary analysis of our results,²⁵ we suggested that there was a first-order alkyl radical loss in our experiments, but now we consider this interpretation to be incorrect. The good fit in graphs such as fig. 7 supports this view, as does further analysis of our initial conclusions.

Line (a) in fig. 8 shows the variation in the methyl radical signal at 216 nm and at relatively low frequency (1 s) with the square root of the photolytic intensity; the near linear relationship is consistent with radical production by photolysis and loss predominantly by mutual reaction. Under each point is shown the number of photolysis lamps used to obtain the result. The measurements taken later in an experiment when there has been considerable consumption of the reactant are those where the photolysis rate with the same number of lamps has fallen. There is obviously no trend with the degree of conversion and, when results with different initial azomethane densities are compared, there is no systematic change either.

Although the best line through the points does appear to extrapolate to a negative intercept, when correction is made for the finite length of the photolysis period a good straight line (b) through the origin is obtained, confirming that only second-order kinetics are significant.

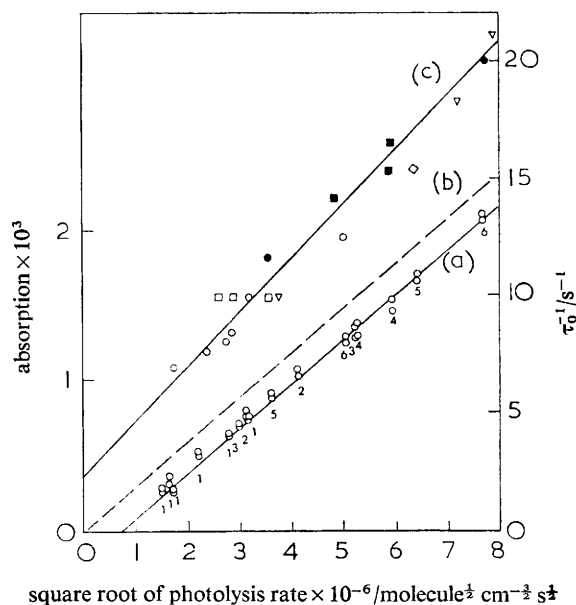


FIG. 8.—The variation of methyl radical absorption at low frequency ($\tau = 1$) and time constant with the square root of the photolytic rate of radical production. Initial azomethane pressure = 2.85 Torr, $N_2 = 150$ Torr. (a) absorption, (b) calculated absorption at infinite period, (c) time constant (τ_0). (The time constants were measured in several different experiments at different substrate densities.)

Line (c) in fig. 8 shows τ_0^{-1} , the reciprocal of the period at which the counting is equal in-phase and in-quadrature, also plotted against the square root of the photolytic intensity. At the higher intensities, there is a good linear relationship but here too there appears to be a deviation from pure second-order behaviour at low intensity, this time leading to a positive intercept. When the two uncorrected lines are compared with fig. 4, however, the deviations in τ_0^{-1} are greater than would be expected relative to those in R_0 . In particular, the intercept of line 4(a'), calculated where there is both a first-order component and a finite photolysis period, has an intercept 3.5 times larger than the intercept in the equivalent plot of τ_0^{-1} . τ_0 is insensitive to the participation of a first-order reaction, but it is sensitive, by its nature being the crossing of two curves, to small errors in measurement. For example, it is possible that the spurious counting at the side of the substrate absorption band is leading to errors when the signal is small. The absorption at τ_0 , when the photolysis rate is 6×10^{12} molecule $\text{cm}^3 \text{s}^{-1}$, is of the order of 2×10^{-4} and τ_0 is apparently 0.14 s instead of the 0.17 s that would be predicted by extrapolation; a spurious count equivalent to an absorption of 4×10^{-5} would account for the error. Measurements of τ_0^{-1} are useful for obtaining a preliminary value for k_2 , but to obtain a more accurate value the full curves of absorption in-phase and in-quadrature must be used.

Further evidence for this interpretation is provided by the graphs of $\ln[R_0]$ against total photolysis, the graphs from which the rates of photolysis are found. As was

seen in fig. 5(a) these are fairly good straight lines over a range in which R_0 changes by close to a factor of 10 (the final azomethane density is 1 % of the initial). If first-order kinetics were significant at the start (say $k_1 = 0.1k_2[\text{CH}_3]$) then the two rates would be equal towards the end of an experiment. The curves would show a significant downwards curvature, but in practice any observed deviation can be accounted for by the attenuation caused by the finite counting period; line (b) in fig. 8 has been corrected in this way and the result approaches closely on exponential decay. The value of R_0 corresponding to each R measured at 1 s is taken from fig. 3(b).

To confirm that the decay in azomethane density could be used to obtain the rate of photolysis, mixtures of azomethane and N_2 were photolysed and the hydrocarbon products examined by gas chromatography. The rate of production of products was equal to that predicted from the rate of photolysis, to within the experimental error (5 %), and 99.9 % of the hydrocarbon produced was ethane. Furthermore, when the N_2 was replaced by O_2 , the formation of hydrocarbon was totally suppressed. No excited states of the azomethane are kinetically significant and, as has been shown before,²⁶ the photolysis may be described by eqn (17)



The measured rate constant is that of the recombination reaction, (18), alone

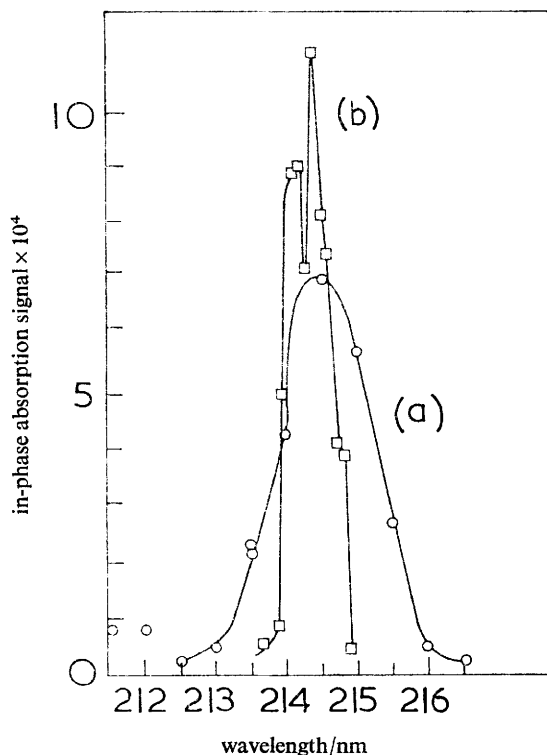


FIG. 9.—Absorption spectrum of perdeutero methyl radicals: 2.8 Torr perdeuteroazomethane, 760 Torr N_2 , $\tau = 1$ s, photolysis rate = 10^{-4} s, slit width (a) 1 mm, (b) 0.1 mm.

PERDEUTERO METHYL RECOMBINATION

The absorption spectrum of perdeuteromethyl radicals is shown at two different resolutions in fig. 9. The deuterated radical is less predissociated and more shape is evident in the band, but with our resolution we cannot resolve the structure and obtain a meaningful absorption coefficient. The absorptions shown in fig. 10,

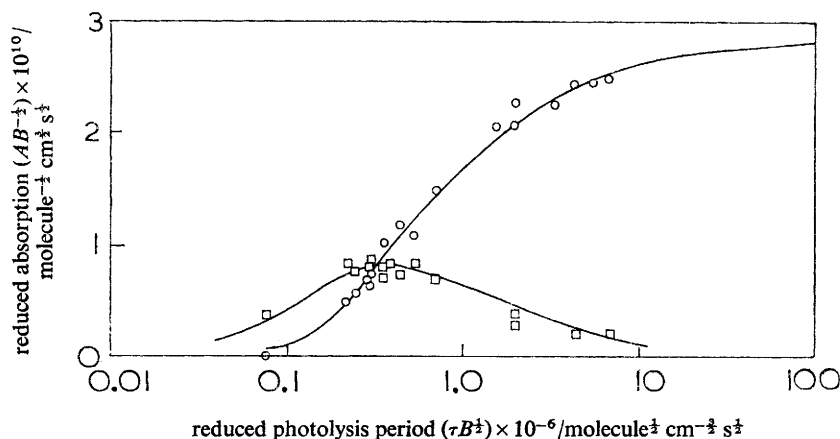


FIG. 10.—The variation in perdeutero methyl radical reduced absorption with reduced photolysis period: initial perdeutero azomethane pressure, 2.8 Torr; 760 Torr N_2 . O, in-phase; □, in-quadrature; slit width 1 mm. Lines drawn for $k = 4 \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$.

where the perdeutero results are presented as reduced absorptions against reduced photolysis periods, are therefore arbitrary, but the time constant is significant. The rate constant obtained is identical within experimental error to that obtained for methyl. Although there may be systematic errors in the method it is concluded that $k_{\text{CD}_3} = (1.0 \pm 0.2)k_{\text{CH}_3}$.

METHYL RECOMBINATION AS A FUNCTION OF TEMPERATURE

The rate of methyl recombination has been measured at four temperatures, 253, 273, 298 and 373 K, and within experimental error the results are identical. Some illustrative results are shown in fig. 11; the individual in-quadrature points are omitted for clarity, but from the in-phase data there is no systematic difference between the results at the different temperatures, *i.e.* both k_2 and the absorption cross-section are unchanged. These results were obtained using successive expansions of the same mixture from the mixing vessel. At 450 K a strongly absorbing non-transient product is being formed, presumably by radical attack on the azomethane. Fig. 12 shows an absorption measurement at that temperature. Apart from the wavelength at which CH_3 absorbs, the apparent negative absorptions are scattered about the line predicted from the rate of change of monitoring intensity. At 216 nm the difference between the absorption and the effect predicted from the change in I_0 and reference voltage arising from product absorption [*cf.* eqn (16)] gives a methyl absorption identical to that expected from the results at other temperatures. Although the product is strongly absorbing, leading to a large superficial effect on the results, the actual rate of CH_3 attack on azomethane must be slow compared with the combination, otherwise the methyl signal would be attenuated. It is concluded that methyl combination at

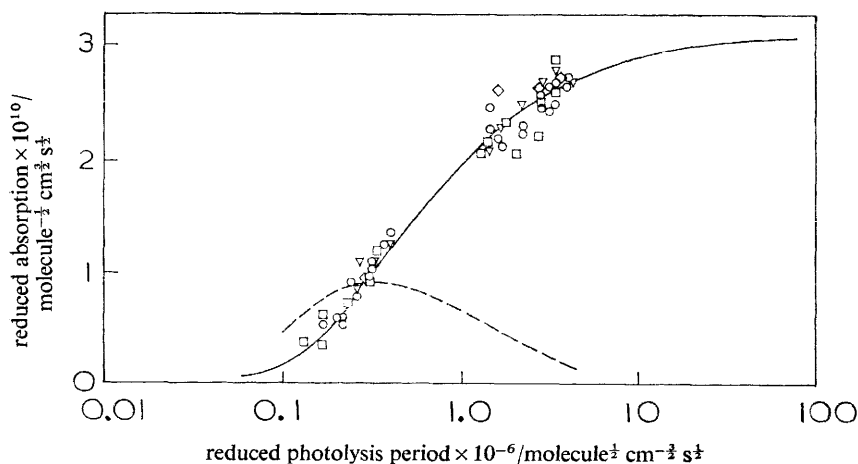


FIG. 11.—Methyl radical reduced absorption as a function of reduced photolysis period at different temperatures: initial azomethane pressure at 298 K = 7.8 Torr; ∇ , 253; \diamond , 273; \circ , 298; \square , 373 K.

450 K cannot be faster than at lower temperatures and is in fact probably the same. The build-up of absorbing products is suppressed by the addition of isobutane, with which methyl radicals react at this temperature, confirming that the products are not formed during the initial photolysis. Furthermore, up to 450 K at least, the thermal decomposition of azomethane is negligible in comparison with the effects of photoly-

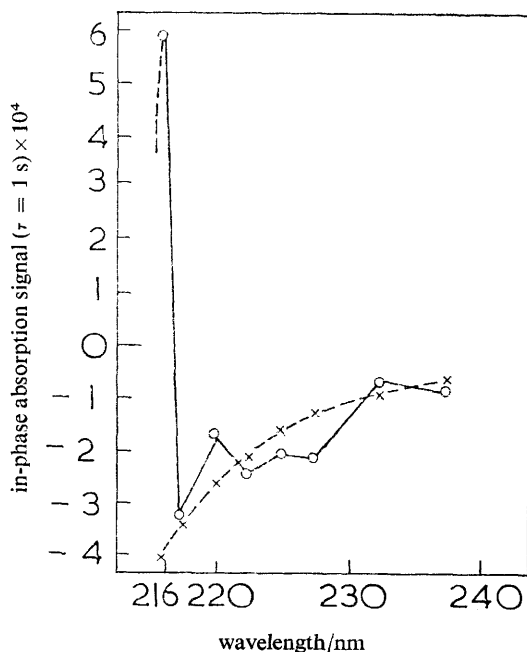


FIG. 12.—Photolysis of azomethane at 447 K: 3.6 Torr azomethane, 700 Torr N_2 , $\tau = 1$ s, photolytic rate of radical production = 3.6×10^{13} molecule $^{-1}$ cm 3 s $^{-1}$. \circ , observed absorption signals; \times , expected from rate of change in monitoring intensity.

sis; if a mixture is left to stand in the dark for an hour or two the radical production at the end of the period is not significantly reduced.

DISCUSSION

The rate constant measured for the recombination of methyl radicals at room temperature is in excellent agreement with results obtained from flash-photolysis in four different investigations.⁷⁻¹⁰ The reaction times and radical densities involved in this work differ by two to three orders of magnitude from those found in flash-photolysis and the agreement should confirm that the rate constant is well established. It also validates our experimental method. The major problem has been to show that there is no first-order radical loss. Even if we have underestimated the presence of such a process, the absolute effect upon the measurement of k_2 will be small (provided the first-order process is not dominant) for it would mean that by ignoring it we have over-estimated the rate of the second order reaction and the rate of photolysis by similar amounts, making the error in the rate constant relatively small. The standard deviation in the values of k which give satisfactory fits to the results from different experiments is $\pm 20\%$. Systematic errors will arise predominantly from any inhomogeneity in the photolysis and from the effects of substrate-induced apparent absorptions. Except for the effect of the latter upon τ_0^{-1} , these are believed to be less than the random error. The electronic timing and switching is orders of magnitude more precise and rapid than the actual photolytic experiment, and errors on this account and from spurious machine-induced signals are negligible.

As found from the rotating sector results,^{14, 3} the rate constant measured for perdeuteromethyl recombination is identical¹¹ to that of methyl at room temperature. A recent flash-photolytic study of the recombination gives a similar ratio, $1 : 0.9 \pm 0.09$.²⁷ Quack and Troe¹⁷ predict a small isotope effect of $1 : 0.77$ with the deuterated recombination slower. Whereas the error limits are such that our results are not sufficiently precise to determine absolute rate constants to the accuracy necessary to test this prediction, the precision in the ratio between two rate constants from identical experiments must be seen from the data in fig. 7 and 10 to be better than 20% . The unreduced time constants are identical when the two azo compounds, azomethane and perdeuteroazomethane, are compared at the same pressure with lamps of the same age, and therefore the comparison is meaningful. As the quantum yield for azomethane photolysis is unity,²⁶ and the light absorption takes place in the N_2 bond, it is unlikely that the photolysis rate is different for ordinary and perdeutero azomethane. There is further evidence that the kinetic isotope effect is also close to unity at higher temperatures. Clark and Quinn²⁸ have measured the effect in the dissociation of ethane at 838 K and find $k_{-2}^D/k_{-2}^H = 1.14$ at 210 Torr ethane equivalent pressure. From this it is calculated that $[k_2^D/k_2^H] = 1.29$, *cf.* the 0.77 predicted by Quack and Troe using Shimonouchi's²⁸ vibrational assignments for ethane (or 1.00, *cf.* 0.60 using Herzberg's data). The isotope effect predictable from the simplest collisional model is $(\mu_{CD_3}/\mu_{CH_3})^{\frac{1}{2}} = 0.91$. Therefore the isotope effect is a small but significant factor different from that predicted by the adiabatic channel model.

It has been difficult to reconcile the measurements of dissociation with recombination at room temperature unless there was a fall in rate at higher temperature, but when Chupka's value²⁹ of ΔH_f^0 for CH_3 is taken, to give ΔH_0^0 for reaction (2) = 87 757 cal mol⁻¹, then there is no conflict. The results of Clark and Quinn on dissociation lead to the following combination rate constants.

$$\begin{array}{ll} \text{At 800 K } k_{1\infty}^H & 3.52 \times 10^{-8} \text{ s}^{-1} \rightarrow k_{-1}^H = 3.7 \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1} \\ \text{900 K } & 1.878 \times 10^{-5} \text{ s}^{-1} \rightarrow 3.8 \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}. \end{array}$$

This work has shown no temperature dependence between 250 and 450 K and it is concluded that this remains true up to at least 900 K. The adiabatic channel model predicts such a small temperature dependence. Although with ethane the high temperature results may be successfully described in terms of RRKM theory with a semi-rigid complex,²⁷ the deficiencies of the RRKM method when applied to alkyl radical recombination/alkane dissociation are well known.^{3, 4} For example, to describe our room temperature isotopic results and the magnitude of the rate constant would call for a totally loose transition state in the recombination, the equivalent of simple collision theory. There have been attempts⁴ to improve the description by identifying the position of the transition state with the position of "minimum entropy" on the potential energy surface, but the activation energy required for dissociation to get a good fit is low. As an alternative, Quack and Troe¹⁷ proposed to identify the adiabatic reaction channels available between reactants and products and then sum the rate over these channels. They demonstrate where their model overcomes some of the traditional difficulties and obtain a good description of fall-off and temperature-dependence. It is concluded, however, from the isotope effect results, that it could be further refined.

The maximum cross-section for methyl absorption 3.2×10^{-17} cm² observed with a resolution of 0.6 nm will be less than the absolute. Quack³⁰ has calculated the absolute value should be 4.2×10^{-17} , assuming that the instrumental dispersion is the one stated by the manufacturers.

Quack has also compared the two CD₃ spectra in fig. 9 and predicts that the absorption cross-section ratio should be 2.85. The observed absorption ratio is 1.65, but this does not take into account the consumption of substrate between the low and subsequent high resolution measurements. It is calculated that the radical density should be 1.5 times less for the latter, giving a ratio of 2.5 which compares very well with the calculation. The maximum cross-section for CD₃ absorption at 1.2 nm resolution obtained from fig. 10 is 3×10^{-17} from which an absolute value of 1.0×10^{-16} may be calculated. This result compares favourably with Quack's results at high temperature.

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(PAPER 5/2249)