J. Chem. Soc., Faraday Trans. 2, 1985, **81**, 613-624

Determination of Absolute Rate Data for the Reaction of Atomic Sodium, $Na(3\,^2S_{1/2})$, with CF_3Cl, CF_2Cl_2, $CFCl_3$, CF_3Br and SF_6 as a Function of Temperature by Time-resolved Atomic Resonance-absorption Spectroscopy at $\lambda = 589$ nm $[Na(3\,^2P_J) \leftarrow Na(3\,^2S_{1/2})]$

By David Husain* and Paul Marshall

Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge
CB2 1EP

Received 13*th September*, 1984

We present a kinetic study of the reactions of ground-state sodium atoms with the molecules CF_3Cl, CF_2Cl_2, $CFCl_3$, CF_3Br and SF_6 over the temperature range 644-918 K. $Na(3\,^2S_{1/2})$ was generated by the low-energy pulsed irradiation of NaI vapour above NaI solid at elevated temperatures in the presence of added reactants and monitored photoelectrically in the 'single-shot mode' by time-resolved atomic resonance absorption of the D lines at $\lambda = 589$ nm $[Na(3\,^2P_J\text{-}3\,^2S_{1/2})]$, unresolved to ensure adherence to the Beer-Lambert law. The photoelectric signals were amplified without distortion, captured, digitised and stored in a transient recorder interfaced to a microcomputer for kinetic analysis. Absolute second-order rate constants for the reaction of sodium with these gases were determined at five temperatures within the overall temperature range, leading to the followin Arrhenius parameters $[k = A\exp(-E/\boldsymbol{R}T)$, errors $1\sigma]$:

	$A/10^{-10}$ cm^3 molecule^{-1} s^{-1}	$E/$kJ mol^{-1}
CF_3Cl	5 ± 3	37 ± 4
CF_2Cl_2	5.6 ± 1.2	18.7 ± 1.5
$CFCl_3$	3.5 ± 0.5	6.1 ± 0.7
CF_3Br	*ca.* 4	<10
SF_6	5.5 ± 1.2	10.3 ± 1.2

These results, including data for CF_4, for which only an upper limit to the rate constant is presented, are compared with analogous results derived previously using sodium diffusion-flame measurements at single temperatures.

The kinetic study of atomic sodium in its electronic ground state, $Na(3\,^2S_{1/2})$, by time-resolved atomic resonance-absorption spectroscopy following pulsed irradiation of alkali-metal halide vapours at elevated temperatures[1] was principally developed to determine absolute second-order rate constants and hence total cross-sections for reaction with molecular halogens.[2-4] One fundamental objective of such measurements was to complement earlier measurements of differential cross-sections derived from molecular beams.[1-5] A further class of halogen-atom abstraction processes undergone by atomic sodium and of interest in this paper concerns reaction with alkyl halides and substituted alkyl halides.[6] Absolute second-order rate constants for such processes have been derived using the diffusion-flame technique, originally developed in 1930 by von Hartel and Polanyi for these particular reactions[7,8] and employed as late as the 1960s by Reed *et al.*[9,10] for the reaction with molecules of the type CF_3Cl, CF_2Cl_2, $CFCl_3$ and CCl_4, and in 1966 for reaction with the molecules CH_3OH and C_2H_5OH.[11] The theory of the diffusion-flame technique, incorporating the combined effects of the diffusion and chemical reactivity of atomic sodium, is complex. The original simplified model of von Hartel and Polanyi,[7] extended by Heller,[12] has been developed mathematically in considerable detail by Reed and Rabinowitch[9,13,14] from the viewpoint of the general equations for continuity in an isothermal system, incorporating the flow of atomic sodium from the nozzle, interdiffusion, back diffusion, wall reaction, the primary atomic reactions of interest and secondary reactions. Notwithstanding these developments, extraction of the fundamental rate constant for the reaction of atomic sodium is model-dependent. A significant limitation of this pioneering technique, so important in the experimental and theoretical development of atomic kinetics in general, is the normal restriction to single-temperature measurements. With this method activation energies are extracted from rate constants measured at a single temperature coupled with assumed values of pre-exponential factors.[15,16] This applies to the study of the reactions of interest in this paper by the diffusion-flame technique.[10]

We describe measurements of absolute second-order rate constants for the reactions of $Na(3\,^2S_{1/2})$ with CF_3Cl, CF_2Cl_2, $CFCl_3$, CF_3Br and SF_6(RX). By contrast with the earlier diffusion-flame measurements, these fundamental rate processes are isolated in real time by the method we have described for the 'single-shot mode' time-resolved resonance-absorption spectroscopic measurements on $Na(3\,^2S_{1/2})$ following pulsed irradiation of NaI in the vapour phase.[17] This experimental system, following our earlier cruder design,[18] avoids complications arising from repetitive pulsing on the same mixture in a static system.[1-4] Further, we have shown that this experimental arrangement, with computer interfacing and a specially constructed high-temperature reactor, permits $Na(3\,^2S_{1/2})$ to be monitored in the time domain, leading to absolute rate data for a temperature range of *ca.* 500-1000 K.[17] Thus, reaction rate constants for $Na(3\,^2S_{1/2})$ with RX are measured as a function of temperature and the Arrhenius parameters are characterised, in particular the activation energies, which are compared with values derived from diffusion-flame measurements at single temperatures. Finally, the slow reaction of $Na(3\,^2S_{1/2})$ with CF_4 is studied in detail over a wide temperature range. However, the resulting rate data exhibit effective Arrhenius parameters that are not in accord with values expected for a single fundamental atomic rate process. Further, the role of secondary processes in diffusion flames with high densities of atomic sodium is considered.

EXPERIMENTAL

The experimental arrangement for monitoring $Na(3\,^2S_{1/2})$ by time-resolved atomic resonance absorption in the 'single-shot mode' following the pulsed irradiation of NaI vapour above NaI solid at elevated temperatures was essentially that employed in our recent investigation of the third-order reaction between $Na+O_2+N_2$ in the temperature range 571-1016 K.[17] A limited number of minor modifications were made to the system, principally to eliminate any significant photolysis of the reactant RX, especially CF_2Cl_2, $CFCl_3$ and CF_3Br in the quartz ultraviolet.[19-21] Hence a Pyrex sleeve was placed around the cylindrical flash lamp to limit photolysis to $\lambda > ca.$ 300 nm. $Na(3\,^2S_{1/2})$ was thus generated from the flash photolysis of NaI vapour in the absorption band centred at $\lambda = 325$ nm.[22] In the same vein this wavelength restriction, eliminating actinic light absorption by the atomic precursor in its strong u.v.-absorption spectrum,[22] coupled with the use of relatively low energies ($E \approx$ 5-40 J), gave rise to initial concentrations of $Na(3\,^2S_{1/2})$ of $<10^{11}$ atom cm^{-3}, as indicated by the degree of resonance light absorption. This in turn eliminated any kinetic effects resulting from secondary reactions following the initial process between Na and RX. This may be contrasted with diffusion-flame measurements where $[\mathrm{Na}(3\,^2S_{1/2})] \approx 2\times10^{13}$ atom cm^{-3} in typical cases, and where secondary reactions are significant (see later). Finally, integration of the light output from the flash lamp, approximated to a black-body radiator of $T = 6500$ °C,[18,23] over the absorption spectra of the reactants indicates that the photolysis of RX is negligible.

Following the pulsed generation of $\mathrm{Na}(3\,^2S_{1/2})$ in the presence of RX and an excess of helium buffer gas, the atomic sodium was monitored by time-resolved resonance absorption of the unresolved D lines at $\lambda = 589$ nm $[\mathrm{Na}(3\,^2P_{1/2,3/2}) \leftarrow \mathrm{Na}(3\,^2S_{1/2})$, $\lambda = 589.6$ and 589.0 nm, $gA = 0.9\times10^8$ and 1.8×10^8 s^{-1}, respectively[24]] derived from a high-intensity, high-current (*ca.* 180 mA) hollow-cathode source.[17,25] The resonance transition was isolated with a grating monochromator (Hilger and Watts Monospek 1000, focal length 1 m, 1200 lines per mm) at large slit widths (*ca.* 2.5 mm), protected by a blocking filter (Wratten filter 21) to eliminate scattered light from the flash at $\lambda <$ *ca.* 530 nm. The resonance-absorption signals were monitored photoelectrically (E.M.I. p.m. tube 9783B, 700 V) and amplified without distortion.[26] The resulting signals were captured in a transient recorder (Data Laboratories DL 902) storing 2048 data points, digitised to an accuracy of 1 part in 256, with a maximum sampling rate of 1 MHz and employed in the A/B mode to measure the attenuated (I_{tr}) and unattenuated (I_0) signals on separate timescales. The resonance-absorption signals were transferred to a microcomputer (Comart CP 200) interfaced to the transient recorder (8PIO parallel interface) and analysed by iterative fitting using a least-squares program to the form described previously:[17]

$$I_{\mathrm{tr}} = I_0 \exp\left[-A \exp\left(-k't\right)\right]. \qquad \text{(i)}$$

k' is the pseudo-first-order rate coefficient for the decay of $\mathrm{Na}(3\,^2S_{1/2})$ and is the prime object of kinetic interest. Eqn (i) describes the form of the resonance-absorption signal for pseudo-first-order kinetic decay of $\mathrm{Na}(3\,^2S_{1/2})$ coupled with the standard Beer–Lambert law. This latter condition has been established from 'curve-of-growth' measurements[18,27] on the unresolved D lines for degrees of light absorption of $<$*ca.* 40%, which is the value employed here. The fitting routine and the advantages of employing eqn (i) compared with the use of standard first-order plots {*i.e.* $\ln[\ln(I_0/I_{\mathrm{tr}})]$ against t} have been described hitherto.[17] Full details of the high-temperature reactor and lamp assembly, together with the vacuum-handling procedure, can be found in our earlier paper.[17] Quoted errors represent one standard deviation. All materials were prepared essentially as described in previous publications [NaI(solid), He, Kr (for the photoflash lamp and the spectroscopic resonance source), CF_3Cl, CF_2Cl_2, $CFCl_3$, CF_3Br, CF_4 and SF_6].[17,18,20,28-30]

RESULTS AND DISCUSSION

The reaction of $\mathrm{Na}(3\,^2S_{1/2})$ with CF_3Cl is taken as an example to demonstrate the nature of the raw data obtained in the present investigation. Fig. 1(*a*) shows the digitised time-variation of the transmitted light intensity at $\lambda = 589$ nm, indicating the decay of resonance absorption by $\mathrm{Na}(3\,^2S_{1/2})$ in the presence of helium alone following the pulsed irradiation of NaI vapour at $T = 695$ K. We have shown hitherto[17,18] that the removal of atomic sodium following its photochemical generation in the presence of a buffer gas is determined by diffusional loss to the walls of the reaction vessel. We have presented a detailed investigation of the diffusion coefficient, $D(\mathrm{Na{-}N_2})$, in our previous paper,[17] including the temperature dependence of this quantity. We have also reported values for $D(\mathrm{Na{-}He})$[18,31] [$D(\mathrm{Na{-}He})$ at s.t.p. ≈ 0.25 cm^2 s^{-1}], although the data were found to be scattered. Whilst further characterisation of the diffusion coefficient of $\mathrm{Na}(3\,^2S_{1/2})$ in He is not pursued here, we may note the kinetic consequence of removal by this pathway. In particular, this leads to the very slow decay rate of $\mathrm{Na}(3\,^2S_{1/2})$ in the absence of added reactant gas and results in dominant removal due to reaction with RX when present, as will become evident, and hence facilitates isolation of the fundamental atomic reaction.

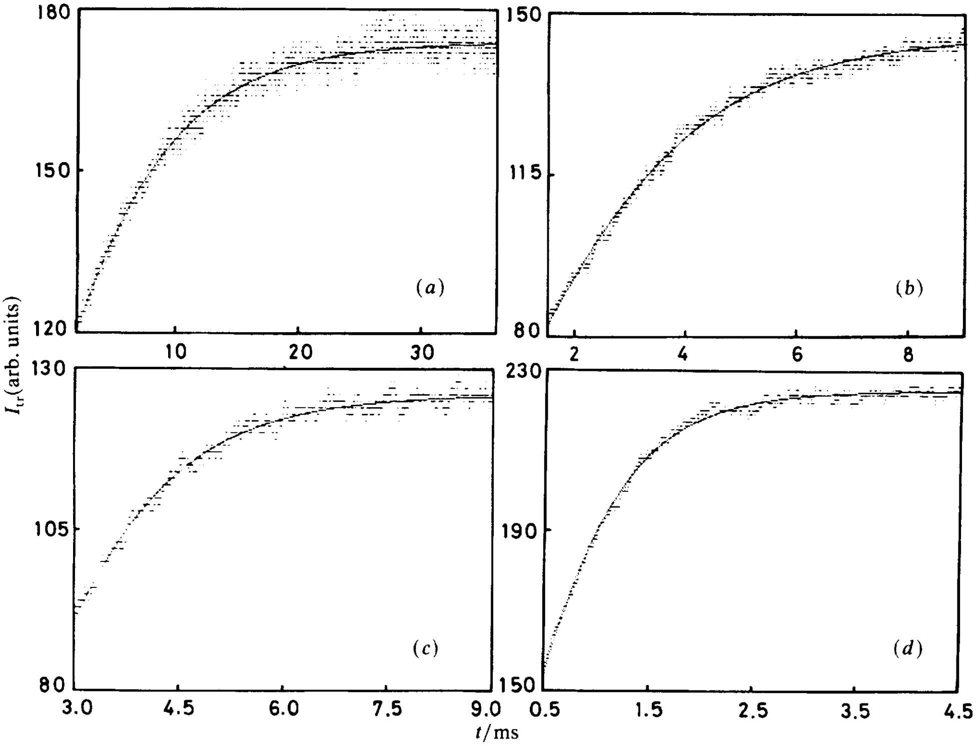

Fig. 1. Examples of the digitised time-variation of the transmitted light intensity (I_{tr}) at $\lambda = 589$ nm [Na($3\,^2P_J$-$3\,^2S_{1/2}$)] indicating the decay of resonance absorption by ground-state sodium atoms in the presence of CF_3Cl and helium buffer gas at various temperatures following the pulsed irradiation of NaI $\{p_{\text{total with He}} \approx 60$ Torr; ::, digitised data points; smoothed curve, computerised fitting to the form $I_{tr} = I_0 \exp[-A \exp(-k't)]\}$.

	$[CF_3Cl]/10^{14}$ molecule cm^{-3}	T/K
(*a*)	0	695
(*b*)	2.9	744
(*c*)	2.9	795
(*d*)	2.8	918

Fig. 1(*b*)-(*d*) show examples of the decay of Na($3\,^2S_{1/2}$) with essentially a constant added concentration of CF_3Cl and with increasing temperature, indicating an increase in the rate. Similar sets of raw data were obtained for the other reactant gases. Fig. 1(*a*)-(*d*) were subject to the fitting routine employing eqn (i) and yielding k', the first-order decay coefficient for Na($3\,^2S_{1/2}$). For a given temperature and total pressure determined by the excess of helium buffer gas, we may describe the removal of Na($3\,^2S_{1/2}$) in the presence of CF_3Cl, for example, by the following rate equation:

$$-\mathrm{d}[\mathrm{Na}]/\mathrm{d}t = k_{\mathrm{diff}}[\mathrm{Na}] + k_{CF_3Cl}[CF_3Cl][\mathrm{Na}] \qquad \text{(ii)}$$

where k_{CF_3Cl} is the absolute second-order rate constant for the reaction

$$\mathrm{Na} + CF_3Cl \rightarrow \mathrm{NaCl} + CF_3. \qquad (1)$$

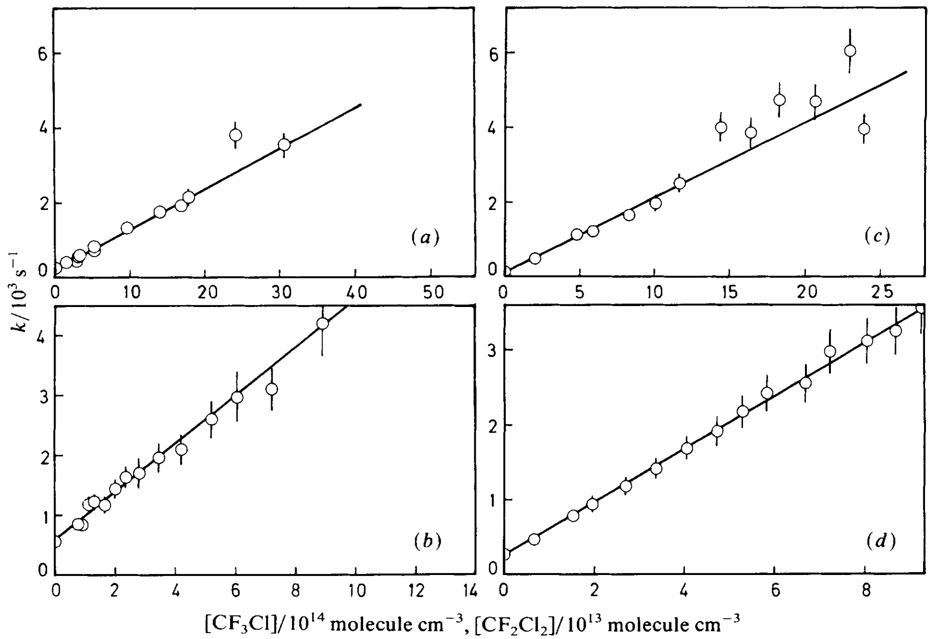

Fig. 2. Variation of the pseudo-first-order rate coefficient, k', for the decay of Na($3\,^2S_{1/2}$) in the presence of CF_3Cl and CF_2Cl_2 at different temperatures [$p_{\mathrm{total\ with\ He}}$: (*a*), (*b*) *ca.* 60 Torr; (*c*), (*d*) *ca.* 35 Torr]. CF_3Cl: (*a*) 744 and (*b*) 918 K; CF_2Cl_2: (*c*) 677 and (*d*) 824 K.

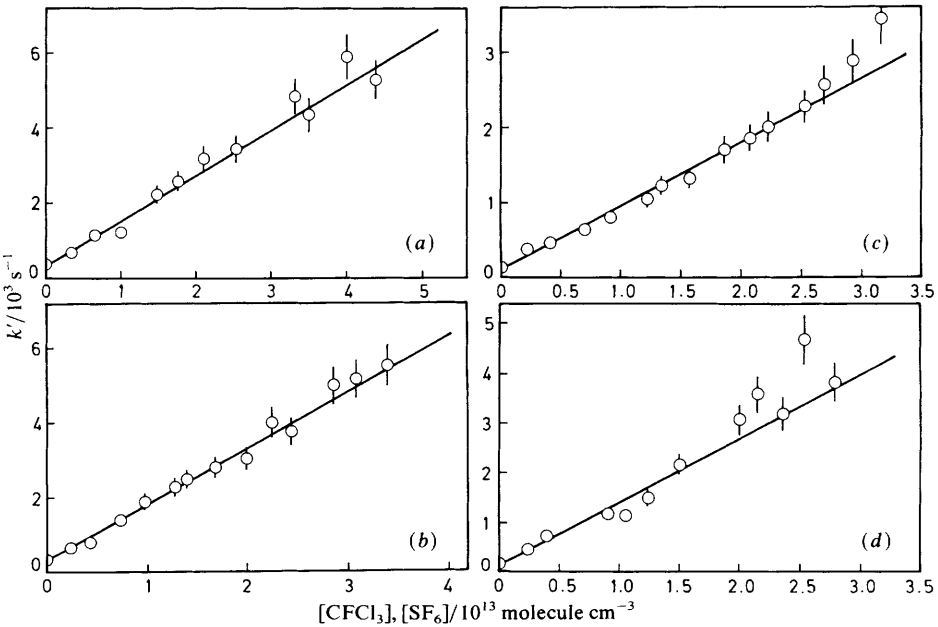

Fig. 3. Variation of the pseudo-first-order rate coefficient, k', for the decay of Na($3\,^2S_{1/2}$) in the presence of $CFCl_3$ and SF_6 at different temperatures ($p_{\mathrm{total\ with\ He}} \approx 36$ Torr). $CFCl_3$: (*a*) 680 and (*b*) 857 K; SF_6: (*c*) 657 and (*d*) 866 K.

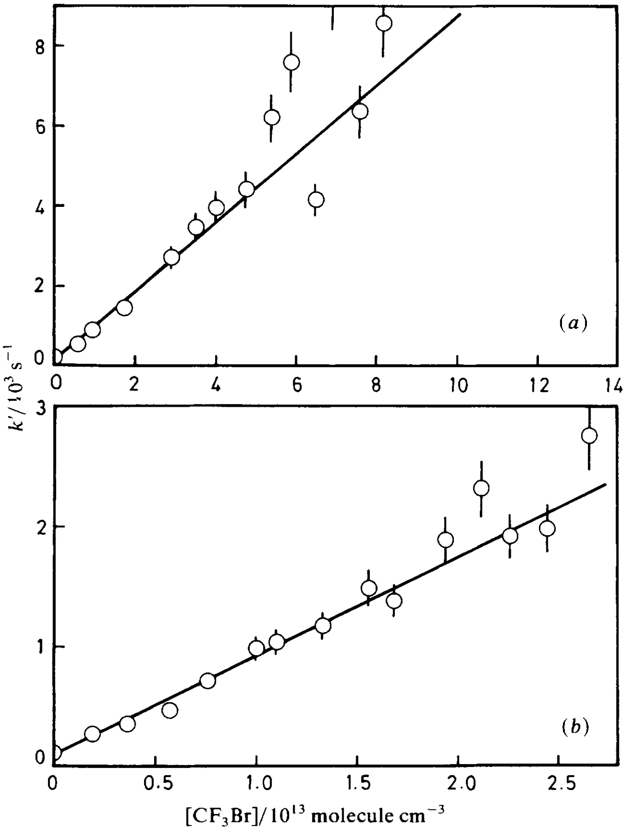

Fig. 4. Variation of the pseudo-first-order rate coefficient, k', for the decay of Na($3\,^2S_{1/2}$) in the presence of CF_3Br at different temperatures ($p_{\text{total with He}} = 35$ Torr). (*a*) 681 and (*b*) 865 K.

Hence, we may write

$$k' = k_{\text{diff}} + k_{CF_3Cl}[CF_3Cl]. \tag{iii}$$

Of course k_{diff}, which is inversely proportional to p_{He}, can be identified with the simplified form of the 'long-time solution' of the diffusion equation for a long cylinder of radius r:[27,32]

$$k_{\text{diff}} \approx 5.81\ D(\text{Na-He})/r^2 \tag{iv}$$

and its value is small compared with $k_{RX}[RX]$ under most conditions. Alternatively, k_{diff} can simply be taken as an empirical constant, namely the intercept in a plot of k' against $[CF_3Cl]$ in particular, or $[RX]$ in general, at a given total pressure with helium.

Fig. 2(*a*) and (*b*) give examples of the variation of k' with $[CF_3Cl]$ at constant total pressure for two of the temperatures used in fig. 1 (744 and 918 K). Hence, the slopes of fig. 2(*a*) and (*b*) yield, respectively, k_{CF_3Cl} ($T = 744$ K) and k_{CF_3Cl} ($T = 918$ K). A similar pair of plots for CF_2Cl_2 for $T = 677$ and 824 K are shown in fig 2(*c*) and (*d*). Removal of Na($3\,^2S_{1/2}$) by CF_2Cl_2 is clearly seen to be more rapid than by CF_3Cl from rough inspection of the abscissae in particular. Fig. 3 shows pairs of plots of k' against $[CFCl_3]$ and $[SF_6]$ for two of the temperatures investigated in each case. Finally, in this context, fig. 4 shows the variation of k'

Table 1. Absolute second-order rate constants (errors 1σ) for the reaction of $Na(3\,^2S_{1/2})$ with CF_3Cl, CF_2Cl_2, $CFCl_3$, CF_3Br and SF_6 at various temperatures determined by time-resolved atomic resonance-absorption spectroscopy at $\lambda = 589$ nm [$Na(3\,^2P_J) \leftarrow Na(3\,^2S_{1/2})$]

T/K	$k_{CF_3Cl}/10^{-12}$ cm^3 molecule^{-1} s^{-1}
695	0.78 ± 0.05
744	1.08 ± 0.05
795	1.88 ± 0.06
853	2.37 ± 0.04
918	3.90 ± 0.16

T/K	$k_{CF_2Cl_2}/10^{-11}$ cm^{-3} molecule^{-1} s^{-1}
677	2.02 ± 0.10
727	2.54 ± 0.10
776	3.27 ± 0.13
824	3.53 ± 0.11
863	4.28 ± 0.20

T/K	$k_{CFCl_3}/10^{-10}$ cm^3 molecule^{-1} s^{-1}
644	1.04 ± 0.10
680	1.21 ± 0.05
726	1.32 ± 0.09
824	1.43 ± 0.08
857	1.49 ± 0.05

T/K	$k_{SF_6}/10^{-11}$ cm^3 molecule^{-1} s^{-1}
611	7.11 ± 0.37
657	8.38 ± 0.27
714	9.3 ± 0.5
786	12.6 ± 1.0
866	12.7 ± 0.7

T/K	$k_{CF_3Br}/10^{-11}$ cm^3 molecule^{-1} s^{-1}
681	8.5 ± 0.6
722	9.45 ± 0.27
865	8.16 ± 0.32

against [CF_3Br] for $T = 681$ and 865 K. In this case alone, no significant temperature dependence of the reaction rate could readily be measured.

Before considering the data in Arrhenius form, it is especially instructive to inspect the variation observed with the second-order rate constants for the different reactant gases over the temperature ranges employed. This is seen in table 1. Thus, whilst a factor of five has been observed in k_{CF_3Cl}, a variation of $<50\%$ is observed for k_{CFCl_3} across a similar temperature range. Of necessity, the reactions must be investigated at elevated temperatures as NaI vapour is the photochemical precursor of $Na(3\,^2S_{1/2})$, and the fractional change in temperature that can be achieved is limited by standard physical constraints. Indeed, it is only the accuracy resulting

Table 2. Arrhenius parameters [$k_{RX} = A \exp(-E/\mathbf{R}T)$, errors 1σ] for reaction of Na($3\,^2S_{1/2}$) with CF_3Cl, CF_2Cl_2, $CFCl_3$, CF_3Br and SF_6 determined by time-resolved atomic resonance-absorption spectroscopy at $\lambda = 589$ nm [Na($3\,^2P_J$) $\leftarrow$ Na($3\,^2S_{1/2}$)]

RX	$A/10^{-10}$ cm^3 molecule^{-1} s^{-1}	E/kJ mol^{-1}
CF_3Cl	5 ± 3	37 ± 4
CF_2Cl_2	5.6 ± 1.2	18.7 ± 1.5
$CFCl_3$	3.5 ± 0.5	6.1 ± 0.7
CF_3Br	*ca.* 4	<10
SF_6	5.5 ± 1.2	10.3 ± 1.2

from the combination of the temperature stability of the reactor we have described,[17] the high-intensity atomic resonance source[17,25] yielding a good signal-to-noise ratio in the I_0 value at $\lambda = 589$ nm[17] and the data analysis resulting from the computer interfacing that permits the small temperature dependences of rate constants such as k_{CFCl_3} and k_{SF_6} to be characterised.

Table 2 lists the Arrhenius parameters resulting from the present investigation. The estimates of A and E for CF_3Br are based on the results for $T = 681$ and 722 K which yield an upper limit for E. Overall, the activation energies for reaction with Na are seen clearly to decrease with increasing Cl-atom substitution proceeding from CF_3Cl to CF_2Cl_2 and $CFCl_3$ (table 2). This is in contrast to activation-energy data derived from single-temperature rate measurements using diffusion flames,[6] namely CF_3Cl (31.0,[33] 38.5[9] and 42.7[10] kJ mol^{-1}), CF_2Cl_2 (37.7-39.8 kJ mol^{-1} [10]) and $CFCl_3$ (36.4-38.5 kJ mol^{-1} [10]). The upper limit for the activation energy for the reaction of Na with CF_3Br (<10 kJ mol^{-1}, table 2) is in accord with the 'single-temperature value' reported from diffusion-flame measurements (9.6 kJ mol^{-1}).[33] Finally, there is sensible agreement between the present result for $E_{act}(SF_6) = 10.3 \pm 1.2$ kJ mol^{-1} and the 'single-temperature value' derived from diffusion flames [$E_{act}(SF_6) = 13.8$ kJ mol^{-1}].[6,15,16]

The Arrhenius A factors observed here (table 2) are significantly smaller than those implicit in the analysis of the diffusion-flame data. The quoted activation energies and the measured 'single-temperature' rate constants from diffusion flames imply the following A factors (in units of 10^{-10} cm^3 molecule^{-1} s^{-1}): CF_3Cl (8.9,[9] 7.3[33] and 8.7[10]), CF_2Cl_2 (18.9[10]), $CFCl_3$ (28.2[10]) and CF_6 (8[6,15,16]). Hodgins and Haynes[33] only quote an activation energy for the reaction between Na and CF_3Br of 9.6 kJ mol^{-1}. This would be consistent with our measured rate constants (table 1) using an A factor of 4×10^{-10} cm^3 molecule^{-1} s^{-1}, which is in good accord with our estimate (table 2).

The alternative kinetic comparison that can be made for the two techniques employs the rate constants directly. Naturally, this reduces the effect of activation-energy differences on account of the relatively high temperatures employed in both types of investigation, diffusion-flame measurements being performed typically in the temperature range 520-590 K.[6] Whilst the comparison of A factors is the more sensitive test on account of a rate extrapolation to infinite temperature using an activation energy, the rate constant is the measured quantity and, in diffusion flames, the Arrhenius parameters the derived quantities. Accordingly, we present a table of rate constants comparing the extrapolated results from our measurements using the Arrhenius parameters (table 2) with those obtained using diffusion flames (table 3).

Table 3. Comparison of second-order rate constants (k_{RX}/cm^3 molecule^{-1} s^{-1}) for the reaction of Na($3\,^2S_{1/2}$) with CF_3Cl, CF_2Cl_2, $CFCl_3$, CF_3Br, SF_6 and CF_4

RX	T/K	k_{RX}
CF_3Cl	520	9.6×10^{-14} [a]
	520	2.3×10^{-13} [a]
	520	8.3×10^{-14} [b] (15, 16)
	548	6.4×10^{-13} [b] (33)
	568	9.2×10^{-13} [b] (33)
	583	1.3×10^{-13} [b] (10)
	586	3.6×10^{-13} [b] (9)
	568	1.7×10^{-12} [b] (33)
CF_2Cl_2	583	1.2×10^{-11} [a]
	583	6.6×10^{-13} [b] (10)
$CFCl_3$	583	9.9×10^{-11} [a]
	583	1.2×10^{-12} [b] (10)
CF_3Br	560	*ca.* 6×10^{-11} [a]
	560	*ca.* 5×10^{-11} [b] (33)
SF_6	520	5.1×10^{-11} [a]
	520	3.3×10^{-11} [b] (15, 16)
CF_4	520	$<2.5\times10^{-16}$ [a]
	520	4.2×10^{-15} [b] (15, 16)

[a] Obtained by Arrhenius extrapolation of rate data derived from time-resolved atomic resonance-absorption measurements at $\lambda = 589$ nm [Na($3^2P_J \leftarrow 3\,^2S_{1/2}$)] (this work). [b] Obtained by 'single-temperature measurements' using sodium diffusion flames.

These is reasonable agreement between the values of k_{RX} extrapolated from our results (table 2) and the rate constants obtained from diffusion flames for the gases CF_3Cl, $CFCl_3$, CF_3Br and SF_6 although, in the case of CF_3Br, it must be stressed that k_{CF_3Br} ($T = 560$ K) attributed to Hodgins and Haynes[33] was calculated using their value for E_{act} (9.6 kJ mol^{-1}) and an assumed A factor of 4×10^{-10} cm^3 molecule^{-1} s^{-1}. The result for k_{CF_3Cl} reported by Reed and Rabinowitch[9] merits further consideration, as those authors included the role of the following secondary processes over and above reaction (1):

$$Na + CF_3Cl \rightarrow NaCl + CF_3 \quad (1)$$

$$Na + CF_3 \rightarrow NaF + CF_2 \quad (2)$$

$$Na + CF_2 \rightarrow NaF + CF \quad (3)$$

$$Na + CF \rightarrow NaF + C \quad (4)$$

$$2CF_3 \rightarrow C_2F_6 \quad (5)$$

$$2CF_2 \rightarrow C_2F_4. \quad (6)$$

These authors[9] quantitatively determined various products and hence isolated reaction (1) from the overall rate of disappearance of atomic sodium. They further concluded that $k_2 = 1.5\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at $T = 583$ K. We have employed this value coupled with standard values for k_5 and course k_1 for computer simulation of the removal of Na. This indicates that secondary processes in our system are

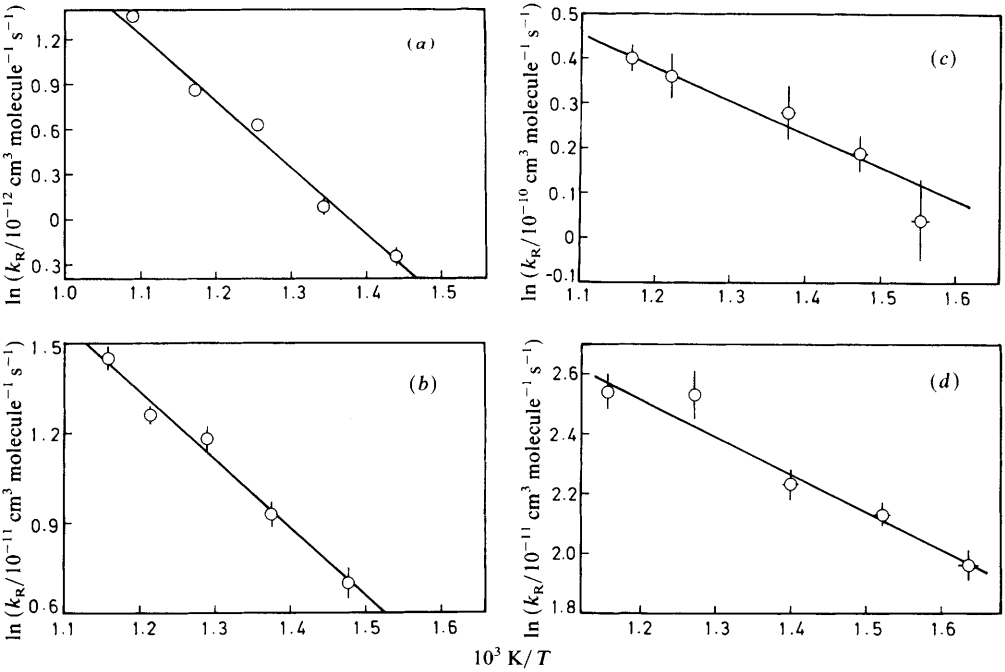

Fig. 5. Arrhenius plots [ln (k_R) against K/T] for the reaction of Na($3\,^2S_{1/2}$) with (*a*)CF_3Cl, (*b*) CF_2Cl_2, (*c*)$CFCl_3$ and (*d*) SF_6.

negligible for [Na] $< 10^{11}$ atom cm^{-3}, consistent with our observations of the degree of resonance light absorption. This concentration of Na is typically two orders of magnitude lower than that normally encountered in diffusion flames.

There is clear disagreement between the rate constants for the gases CF_2Cl_2 and CF_4. The quality of our results for CF_2Cl_2 over a wide temperature range is apparent from fig. 2 and 5. In the case of CF_4 we have carried out two series of kinetic measurements at five temperatures from 767 to 924 K employing photolysis of NaI through both quartz ($\lambda >$ *ca.* 200 nm) and Pyrex ($\lambda >$ *ca.* 300 nm). Consistent sets of data of the type indicated in fig. 2-4 were obtained, with the results for the two-wavelength photolysis regimes in good agreement, and yielding Arrhenius plots of a quality indicated for the other gases in fig. 5. Unfortunately, these yielded the Arrhenius parameters $A = (8 \pm 4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and $E = 35 \pm 3$ kJ mol^{-1}. The A factor is clearly approximately three orders of magnitude too low for reactions of this type. Of course, if the activation energy for the reaction between Na and CF_4 is $\gg 35$ kJ mol^{-1} the observed activation energy could be attributed to an impurity. The observed apparent A factor, coupled with genuine A factors for other similar reactions listed in table 2, would indicate that this impurity is at a level of *ca.* 0.1%. The stated purity of the CF_4 (Matheson, minimum purity 99.7%, air 0.2%, H_2O 0.005%, hydrocarbons 0.005%) is consistent with this, although the starting material was purified by various means. For the reactants investigated here, only reaction with CF_4 involves an endothermic process:[34,35]

$$\mathrm{Na + CF_4 \rightarrow NaF + CF_3}, \qquad \Delta H = 29 \text{ kJ mol}^{-1}. \tag{7}$$

This can be compared with the thermochemistry of reaction (1) of $\Delta H = -154$ kJ mol^{-1}, where the reaction is characterised by an activation energy of

37 ± 4 kJ mol^{-1} (table 2), in close agreement with the apparent activation energy observed with CF_4. CF_3Cl was not detected in the CF_4 sample although the level of impurity would not need to be high to account for the observed results. Notwithstanding our quotation of an upper limit for k_{CF_4}, the result obtained from diffusion flames is concluded to be too large (table 3),[15,16] presumably on account of secondary processes of the type encountered with CF_3Cl with the high atomic sodium densities present in such flames.

In conclusion, there is a broad measure of agreement, with exceptions, between the present results when expressed as rate constants for reaction between atomic sodium and RX and those determined from single-temperature measurements on diffusion flames. This is striking considering the complexity of the pioneering diffusion-flame technique and the simplicity of the time-resolved measurements, which permit isolation of the fundamental atomic reactions of sodium. This agreement, however, is to some extent fortuitous as seen from the disagreement between activation energies for reaction (table 2),[6] whose effects are significantly removed when reflected through the magnitudes of rate constants at high temperatures. The extent to which secondary processes in the diffusion flames are significant for reactants other than CF_3Cl[9] requires at least modelling calculations in individual cases. Whilst the present results describe the first direct time-resolved determinations of rate constants for the fundamental reactions of atomic sodium with these halides, and also as a function of temperature to an accuracy that permits characterisation of the Arrhenius parameters, it is noteworthy that the only data with which we may make a direct comparison at present were derived from modifications of a pioneering technique reported in 1930.

We thank the Ministry of Defence for a research grant, together with the S.E.R.C. for a CASE Studentship held by P.M. We thank Dr J. M. C. Plane for helpful advice and discussion. Finally, we express our gratitude to Dr D. E. Jensen and Dr G. A. Jones of the Propellants, Explosives and Rocket Motor Establishment (Wescott, Buckinghamshire) for their continued encouragement of this work.

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