Reactions Forming Electronically-excited Free Radicals Part 1.—Ground-state Reactions Involving NF₂ and NF Radicals

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Atomic resonance absorption in the far vacuum ultraviolet and atomic resonance fluorescence have been used to investigate the kinetics of primary and secondary processes in the overall reaction of H ²S atoms with NF₂ radicals from 298 to 550 K. Rate constants for the following elementary reactions have been determined directly $[k^{298}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (1\sigma)]$:

H+NF₂ → HF+NF;
$$k_1 = (1.5 \pm 0.2) \times 10^{-11}$$
;
O+NF₂ → NF+FO; $k_5 = (1.8 \pm 0.9) \times 10^{-12}$;
N+NF₂ → NF+NF; $k_8 = (3.0 \pm 1.2) \times 10^{-12}$.

The overall $H+NF_2$ reactive system, containing H_2 , is characterised as a self-propagating chain reaction, in which the chain carriers are H, NF and F. Ground-state N ⁴S atoms are formed by the reaction H+NF, although these atoms play only a minor role in propagating the overall $H+NF_2$ chain reaction. Computer modelling of the H and N atom profiles was used to obtain values for k_4 and k_2 :

H+NF → HF+N;
$$k_4 = (2.5 \pm 0.5) \times 10^{-13}$$
;
NF+NF → N₂+2F; $k_2 = (7.0 \pm 3.5) \times 10^{-11}$.

Thus, the predominant decay channel for NF radicals is through rapid bimolecular disproportionation to give $N_2 + 2F$.

Bimolecular reactions forming electronically-excited products which chemiluminesce are rare. Only a few, out of the many sufficiently excergic elementary reactions, are found to emit radiation in the spectral range 0.2-1.0 μ m. However, many excergic reactions result in the formation of vibrationally-excited products, which may emit infrared chemiluminescence.

Far fewer reactions result in the formation of electronically-excited product molecules. Such reactions are of two types: (a) "dark" reactions, where optical transitions out of the excited state are forbidden and (b) chemiluminescent reactions, involving allowed transitions. Dark reactions are of potential importance in providing energy transfer agents, such as the formation of metastable CO $a^3\Pi$ in the reaction of Ar* ${}^3P_{2,0}$ atoms with ground-state CO₂ $X^{1}\Sigma_{g}^{+}$ molecules.^{1, 2}

A number of the known chemiluminescent reactions involve optical transitions which are only partially allowed. In these cases, the excited states often are very inefficiently quenched, thus allowing the build-up of relatively large steady concentrations of excited states; in consequence, chemiluminescence can be observed.

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Examples include the metastable singlet states of O_2^{3} and the same states of the nitrogen-halogen NX radicals, where X = F, Cl and Br. Thus, the lower-energy $a^{1}\Delta - X^{3}\Sigma^{-}$ transitions and the higher-energy $b^{1}\Sigma^{+} - X^{3}\Sigma^{-}$ transitions are partially-forbidden. The b-X emissions of NCl and NBr in the red were produced in the exoergic reactions of Cl or Br atoms with N₃ radicals; the N₃ radicals were formed from chlorine azide, ClN₃, by reaction with atoms.⁴

Both the a-X near infrared emission and b-X green emission of NF are radiated in the chemiluminescent reaction of H atoms with NF₂ radicals ^{5, 6}

$$H + NF_2 \xrightarrow{\kappa_1} HF + NF.$$
(1)

The band origins of the (0–0) vibrational transitions of NF(a-X) and NF(b-X) are at wavelengths of 528 and 874 nm, respectively.⁷

On indirect evidence, it has been suggested ⁷ that reaction (1) forms mainly or entirely the excited $a^1\Delta$ state of NF, with production of the ground $X^3\Sigma$ state being a minor channel. If this suggestion is correct, it may be possible to create a population inversion between the $a^1\Delta$ and $X^3\Sigma^-$ states. Another possible mechanism favouring an inversion would be rapid depletion of ground (triplet) state NF, through reactions which are fast in comparison to those of excited (singlet) state NF. For example, Herbelin ⁸ has hypothesized that bimolecular disproportionation of NF radicals *via* reaction (2) may be faster for triplet NF than for singlet NF radicals:

$$NF + NF \rightarrow N_2 + 2F.$$
 (2)

If small amounts of NF₂ are added to a stream of H atoms, the green NF chemiluminescence is dominated by yellow emission, which has been identified as the N₂ $B^3\Pi_g - A^3\Sigma_u^+$ First Positive system.⁵ The precursor of the $B^3\Pi_g$ state of N₂ in the H+NF₂ system is unclear, however.

The H+NF₂ reaction therefore is an extremely rich source of excited states, which has implications for the possible usefulness of this reaction system in the field of chemical lasers. If an inversion on the $a^1\Delta$ state of NF is achievable, the a-Xtransitions could form an electronic transition laser, provided that the lifetime of the $a^1\Delta$ state is short enough (e.g., < 1 ms). Alternatively, if the $a^1\Delta$ state of NF is long-lived (> 1 ms), this state could serve as an energy transfer agent, similar to $O_2 a^1\Delta_{g}$, for excitation of a more highly-allowed transition of another species. An example is electronic energy transfer from NF $a^1\Delta$ to Bi atoms, which has been reported by Capelle *et al.*¹⁰

The kinetics of the primary and secondary steps in the $H+NF_2$ system have not been investigated previously. Indeed, the nature of the elementary steps involved has been mainly uncertain. It is clear from the above comments that the reactions involving ground and excited states of NF are coupled together to a large extent. In the present work, the kinetics of reactions of both excited and ground states have been investigated. The present paper concerns reactions involving ground-state species, with reference to the rate constants for elementary reactions of NF₂ with atoms. Also the chain reaction between H₂ and NF₂ radicals has been investigated. A forthcoming paper ¹¹ will be concerned with the kinetic behaviour of ground and excited nitrogen atoms formed in the reaction of H atoms with NF radicals.

EXPERIMENTAL

Detection of free atoms by atomic resonance absorption and fluorescence was used to study the kinetics of reactions of NF_2 radicals with ground-state atoms in a discharge-flow system. Some complementary measurements were made with a mass spectrometer.

Resonance absorption with a windowless cell ¹²⁻¹⁶ was particularly useful in measuring relatively high concentrations of H atoms ($\approx 10^{13}$ cm⁻³) using the Lyman- β line at 102.5 nm, which has an oscillator strength $f_{ik} = 0.0791.^{17}$ Resonance fluorescence was employed to measure lower concentrations of H, O and N atoms. Also, concentrations of H atoms below 10^{12} cm⁻³ can be conveniently measured using absorption at the Lyman- α line at 121.6 nm, which has an *f*-value of 0.4162.¹⁷

Two separate discharge-flow systems, one with an integral resonance absorption cell¹⁶ and the other with an integral resonance fluorescence cell, were used in this study.

RESONANCE ABSORPTION SYSTEM

The resonance absorption system consisted of a resonance lamp, a buffer volume and a monochromator and photon-counting system.¹⁶ The lamp was a 2.45 GHz discharge in purified helium (B.O.C.), to which were added traces of nitrogen and oxygen. The monochromator was a 1 m normal-incidence type; the use of this instrument and the photon-counting system has been described previously.¹⁶ A 600 line mm⁻¹ grating overcoated with Pt and blazed at 90 nm was used in the monochromator.

The system was of a windowless configuration, $^{12-16}$ in which collimated hole structures replaced conventional solid windows. This apparatus facilitated work below 120 nm and was essential below the LiF cut-off near 105 nm.

The buffer volume was a flow cell, which separated the absorption cell from the entrance slit of the monochromator. It was pressurized with pure argon (to, typically, 1.4 Torr) in order to inhibit the flow of corrosive reagents from the flow tube (typically at 0.9 Torr) to the monochromator through the collimated hole structure.¹²⁻¹⁶

The Pyrex flow tube (40 cm \times 2.6 cm i.d.) contained eight coaxial jets, located at distances between 2 and 33 cm from the centre of the absorption cell. The linear flow velocity was $\leq 2900 \text{ cm s}^{-1}$.

RESONANCE FLUORESCENCE SYSTEM

The resonance fluorescence system also consisted of a resonance lamp, flow tube and monochromator. The lamp is described below. However, the monochromator was a 1.5 m Czerny–Turner type (Jarrell-Ash 75-100). The grating was aluminized and over-coated with magnesium fluoride and was blazed at 500 nm in the first order. It was operated in the fourth order to disperse the N, O and H transitions from 120 to 130 nm. F.w.h.m. resolution was better than 5 pm, or a factor of 10 better than that of the normal-incidence monochromator. The detector was a solar-blind photomultiplier tube (E.M.R. 541G-08-18) with a CsI photocathode. Detection of signals was by photon counting.

The resonance fluorescence cell employed MgF_2 windows and was designed for minimum scattered light.¹¹ The flow tube was similar in design to the first one described, but was operated at lower linear flow velocities (typically 1500 cm s⁻¹).

PRODUCTION OF NF_2 RADICALS

NF₂ radicals were formed by the low temperature thermolysis of tetrafluorohydrazine.¹⁸ The low energy of the N—N bond (93 ± 4 kJ mol⁻¹) in N₂F₄, compared with that of the N—F bond (≈ 280 kJ mol⁻¹), indicates that N₂F₄ in a furnace at 500 K will consist almost entirely of NF₂ radicals. At lower temperatures, outside the furnace, the NF₂ could recombine rapidly.^{19, 20} To minimize recombination, heating coils were wound around the inlet tubing connected to the flow tube jets (see fig. 1).

In view of the possibility of NF₂ radicals recombining in any insufficiently heated parts of the inlet jets (*e.g.*, within the flow tube), checks were made for the presence of N₂F₄ in the flow tube, using a quadrupole mass spectrometer, which directly samples stable species.

The N₂F₄ was used from a cylinder (Air Products Research Grade, > 99 %) without further purification. For kinetic studies, it was diluted with purified argon. The flow rate of the N₂F₄+Ar mixture was monitored using a transducer-type mass flow meter (Hastings H-5M).



FIG. 1.—Heated inlet manifold for the formation of NF₂ radicals.

PRODUCTION OF GROUND-STATE H²S, N⁴S AND O³P ATOMS

Ground-state H ²S, N ⁴S and O ³P atoms were produced by a microwave discharge in flows of 0.5 mol % of H₂, N₂ or O₂, diluted with purified argon (B.O.C. High Purity Grade). Purification of cylinder argon was effected with a molecular sieve trap at 198 K. No impurity H, N or O atoms could be detected by resonance absorption, after the purified argon alone had been submitted to a microwave discharge. However, traces of H and O atoms ($\approx 10^{11}$ cm⁻³) were detected in these discharge products, using the more sensitive technique of resonance fluorescence.

RESONANCE LAMPS

The resonance absorption lamp was a simple flowing type, fitted with a collimated hole structure.¹³ The resonance fluorescence lamp was fitted with a MgF₂ window; it employed a simple tube collimator in order to optimize the ratio of fluorescence intensity to scattered-light intensity, whilst preserving adequate fluorescence intensity.²¹ The lamp carrier gas was helium or argon, both of which were purified, as indicated above. The Lyman- α line of H at 121.6 nm is emitted so intensely that a discharge in purified carrier gas proved to be a satisfactory source of unreversed Lyman- α radiation. In the case of the Lyman- β line of H at 102.5 nm and of the O and N atom lines, a trace (< 0.1 mol %) of molecular gas (H₂, N₂ or O₂) was added to the carrier gas in order to excite resonance lines of adequate intensity.

RESULTS

dissociation of N_2F_4 to $2NF_2$ radicals

The absence of undissociated N_2F_4 in NF_2 radicals in the flow tube was verified mass spectrometrically. At ion-source electron energies of 70 eV, both NF_2 and N_2F_4 give NF_2^+ ions and N_2F_4 has a small parent peak. However, H atoms react rapidly with NF_2 radicals, but not with N_2F_4 molecules. Thus, on the addition of excess H atoms to the flow tube to react with all the NF_2 present, any residual NF_2^+ signal at m/e = 52 would indicate the presence of N_2F_4 in the flow tube. No significant NF_2^+ signal was observed under these conditions, when N_2F_4 was introduced to the H atom flow through any of the heated flow tube inlets. Based on the limit of detection of the mass spectrometric technique employed, it is concluded that at least 92 % of the N_2F_4 was present as NF_2 radicals in the flow tube.

DETERMINATION OF ATOM CONCENTRATIONS BY RESONANCE ABSORPTION AND FLUORESCENCE

LAMP DIAGNOSIS

In order to obtain maximum sensitivity in resonance absorption, it is necessary to ensure a non-reversed atomic line source. Once the profile of the source line is known, a curve-of-growth relating absorbed energy to atom concentration may be constructed, based on the oscillator strength f_{ik} for the relevant transition.^{16, 22}

Techniques for verifying the absence of self-reversal are straightforward when the atomic transition is a resolvable multiplet, as in the cases of the N $3s^4P_J$ - $2p^3$ 4S triplet at 120.0 nm and the O $3s^4S-2p^4 \, {}^4P_J$ triplet near 130.4 nm. In such cases, the relative emission intensities of the component lines of the triplet in the lamp provide a criterion for self-reversal.²¹ This approach was used in the present work on N and O transitions and has been described previously.14, 16

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FIG. 2.—Curve-of-growth for H atom resonance fluorescence. Plot shows the variation of I_F/I_S against [H], where $I_{\rm F}$ is the fluorescence intensity and $I_{\rm S}$ is the scattered light intensity, at 121.6 nm (Lyman- α).

Tests for reversal of the Lyman- α 2p-1s transition of H at 121.6 nm present a tricky diagnostic problem, because no other resonance line of H is accessible within the conventional vacuum ultraviolet spectrum. Also, the Lyman- α line is exceptionally sensitive to self-reversal. However, the windowless configuration permitted access to the Lyman- β 3p-1s transition of H at 102.5 nm; the f_{ik} values of both the Lyman- α and Lyman- β lines are known accurately.¹⁷ The ratio of absorption intensities by each line for the same H-atom concentration can be used to detect lamp reversal. The relevant expressions have been presented in ref. (16) and elsewhere. This approach is based on the fact that the Lyman- β line is much less affected by self-reversal than is the Lyman- α line, since the f_{ik} value of the former line (0.0791^{17}) is much smaller than that of the latter line (0.4162^{17}) . In the present experiments, the hydrogen content of the resonance lamp was reduced until the ratio of absorption intensities in Lyman- α and Lyman- β reached the theoretically-expected magnitude for the particular value of [H] employed.

CURVE-OF-GROWTH FOR RESONANCE ABSORPTION

Several groups ^{13-16, 22, 23} have used the result that a Doppler model may be used to represent the line profile of atomic resonance radiation emitted from a lowpower microwave-excited lamp. In this model, T_s is the effective temperature of the lamp plasma, with $\alpha^2 = T_s/T_a$, where T_a is the temperature of the (Doppler) absorber, normally at 298 K. Fig. 1 of ref. (16) shows typical curves-of-growth relating fractional absorption $A = I_{abs}/I_0$ to optical density k_0l or the proportionally-related atom concentration, based on this model.

A value of 1.8 for α has been found in previous work of this group on the N and O atom transitions ^{14, 16} used in the present study. We undertook to verify the assumed α -value of 1.8 for the H-atom lines and thus to obtain an experimental curve-of-growth for H; this curve-of-growth is inherently more satisfactory than one based on calculations from a model. For this purpose, relatively high H atom concentrations were titrated with NO₂, in order to calibrate fractional absorption A against [H]. The titration reaction (3) is rapid,^{21, 24, 25}

 $H + NO_2 \rightarrow OH + NO; k_3^{298} = (1.3 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$ (3)

Values of A determined in this way agreed well with those based on the calculated curve-of-growth with $\alpha = 1.8$.

CURVE-OF-GROWTH FOR RESONANCE FLUORESCENCE

Lamp self-reversal is not of critical importance in the determination of atom concentrations by resonance fluorescence. Indeed, the optimum signal-to-noise ratio is usually obtained by means of a trade-off between self-reversal and lamp intensity, both of which increase as a function of added molecular gas concentration. Using this approach, a calibration of Lyman- α fluorescence intensity against [H] was carried out using the H+NO₂ titration, with extrapolation to zero intensity. As a check of the completeness of the H+NO₂ reaction, the extent of reaction was calculated for each value of [NO₂] added, using the rate constant of ref. (21), (24) and (25).

Fig. 2 shows the results, in the form of a plot against [H] of $I_{\rm F}/I_{\rm S}$, where $I_{\rm F}$ is the fluorescence intensity and $I_{\rm S}$ is the scattered light intensity. Data were included only for > 95 % consumption of added NO₂. A proportional relationship between $I_{\rm F}$ and [H] was observed up to H atom concentrations $\leq 1.5 \times 10^{12} \,\mathrm{cm^{-3}}$, in agreement with our previous work.^{21, 24}

The flattening of the curve of fig. 2 near $[H] = 5 \times 10^{12} \text{ cm}^{-3}$ is due to strong selfabsorption by H ²S atoms of resonance fluorescence. The data of fig. 2 indicate that detection of H atoms by Lyman- α fluorescence is very insensitive for $[H] > 3 \times 10^{12}$ cm⁻³, using a path length of a few cm for absorption of lamp radiation.

KINETIC RESULTS

The atom-plus-radical reactions $H+NF_2$, $N+NF_2$ and $O+NF_2$ were studied kinetically using the fixed observation point method. A reaction was initiated at one of various inlets along the flow tube, by introducing reagent at that inlet into the atom flow. The change in atom concentration was then observed at a fixed observation point downstream, which in this work was the resonance absorption or fluorescence cell. For reactions of an atom with a molecule, namely $A+BC \rightarrow AB+C$, the first-order decay rate of atoms A, measured at the fixed observation point, is independent of concurrent first-order processes such as wall removal of $A.^{26-28}$ Thus, a

pseudo first-order race expression may be used to find k, if $[BC]_0 \ge [A]_0$, then

$$\ln ([A]_0/[A]_t) = k[BC]t = k't.$$

The stoichiometry of the reaction need not be known, unless atoms react rapidly with a product of the primary reaction.

$H+NF_2$ REACTION

Resonance fluorescence detection of H at Lyman- α was used to determine the rate constant k_1 for the H+NF₂ reaction (1) from 298 to 550 K,

$$H + NF_2 \xrightarrow{s_1} HF + NF; \qquad \Delta U_{298}^\circ \simeq -280 \text{ kJ mol}^{-1}. \tag{1}$$

An excess of NF_2 over H was used in order to minimize any effect of the secondary reaction (4) upon the observed rate of depletion of H atoms:

$$H + NF \xrightarrow{k_4} HF + N; \qquad \Delta U_{298}^\circ \simeq -134 \text{ kJ mol}^{-1}.$$
(4)

In fact, results on k_4 (described below) show that $k_4/k_1 \ll 1$ at 298 K and reaction (4) would be unimportant even with low values of initial stoichiometry $[NF_{2}]_0/[H]_0$. Thus, the rate constant k_1 was derived from the following simple rate equation :

$$\ln ([H]_0/[H]) = k't = k_1[NF_2]t.$$

Fig. 3 shows typical data for the first-order decay of H atoms in the presence of excess NF₂ at 298 K. The ranges of initial concentrations were as follows: $10.1 \ge [H]_0 \ge 3.0 \times 10^{11} \text{ cm}^{-3}$ and $18.3 \ge [NF_2]_0 \ge 1.8 \times 10^{13} \text{ cm}^{-3}$. [H₂]₀ was between 2.7 and $2.9 \times 10^{12} \text{ cm}^{-3}$. The mean ratio $[NF_2]_0/[H]_0$ was 11.3. Fig. 4(*a*) shows a summary plot of the 55 independent determinations of the pseudo first-order rate constant k' against $[NF_2]_0$ at 298 K. Similar summary plots for determinations at 421 K (16 measurements), 471 K (26 measurements) and 550 K (14 measurements) are presented in fig. 4(*b*)-(*d*). In all cases, decay of H atoms was verified to be first-order with $[NF_2]$.



time/ms

FIG. 3.—First-order decay of [H] in the H+NF₂ reaction. Typical data are shown for [H₀] $\approx 5 \times 10^{11} \text{ cm}^{-3}$; pseudo first-order conditions with $[NF_2]_0/[H]_0 \ge 1$. $[NF_2]_0/10^{12} \text{ cm}^{-3}$ as follows: (a), 3.0; (b) 3.8; (c) 5.8; (d) 8.2; (e) 10.2.

The rate constants k_1 were determined at each temperature, after making small corrections (≤ 10 %) for consumption of NF₂. The resulting mean values of $k_1 (10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, 1\sigma)$ were as follows: $(1.5\pm0.2) 298 \text{ K}$; $(1.6\pm0.2) 421 \text{ K}$; $(1.6\pm0.2) 471 \text{ K}$ and $(1.7\pm0.4) 550 \text{ K}$. An Arrhenius expression was obtained for these data:

 $k_1 = (1.9 \pm 0.5) \times 10^{-11} \exp \left[-(30 \pm 50)/T\right];$

thus, the rate constant for reaction (1) showed no significant temperature dependence.

$O+NF_2$ reaction

Detection of O ${}^{3}P_{J}$ atoms was by means of resonance fluorescence in the ${}^{3}S-{}^{3}P_{1}$ line at 130.5 nm. A proportional dependence of $I_{\rm F}$ upon (total) oxygen atom concentration has been found up to at least 3×10^{12} cm⁻³.^{29, 30} Typical [O]₀ was 1.5×10^{12} cm⁻³ in the present studies, with [NF₂]₀ in the range 0.56-7.86 $\times 10^{13}$ cm⁻³ and a mean value of 23.5 for [NF₂]₀/[O]₀. Rate measurements were made only at 298 K.



Fig. 5 shows typical logarithmic decay plots, in agreement with the expected firstorder dependence upon [O]. Table 1(*a*) shows a summary of the data, in the form of a listing against $[NF_2]_0/[O]_0$ of the observed second-order rate constant $k_5^{app} = -[NF_2]^{-1} d\ln [O]/dt$. Although there is appreciable scatter in the data, there is a tendency for k_5^{app} to decrease with increasing $[NF_2]$. Limiting values for k_5^{app} were : 3.41×10^{-12} based on data with low $[NF_2]_0/[O]_0 \leq 16$ and 1.77×10^{-12} based on data with high $[NF_2]_0/[O]_0 \geq 30$. These results suggest that there may be a change in $O:NF_2$ stoichiometry with $[NF_2]_0/[O]_0$. With low $[NF_2]_0/[O]_0$, a 1:3 stoichiometry for NF₂:O consumption would result, if the relatively slow first reaction (5) is followed by faster steps (6) and (7), thus giving low stationary values of [NF] and [FO]:

$$O + NF_2 \xrightarrow{k_s} NF + FO$$
 (5)

$$O + NF \rightarrow NO + F$$
 (6)

$$O + FO \xrightarrow{k_7} O_2 + F.$$
 (7)



Although no data on k_6 are available, k_7 is known to be in the order of 10^{-11} cm³ molecule⁻¹ s⁻¹ at 298 K.³¹ At sufficiently high values of $[NF_2]_0/[O]_0$, reaction (5) would predominate, thus giving 1:1 stoichiometry and $k_5 = k_5^{\text{app}}$ under these conditions. Based on this interpretation, we assign k_5 to be 1.8×10^{-12} cm³ molecule⁻¹ s⁻¹, from data with $[NF_2]_0/[O]_0 \ge 30$. Error limits of $\pm 50 \%$ are estimated for k_5 , in light of the tentative nature of the stoichiometry arguments presented above for the O+NF₂ reaction.

Resonance absorption was also used to measure k_1 and k_5 , giving results of lower accuracy than those obtained using resonance fluorescence. However, agreement was within a factor of two.



time/ms

FIG. 5.—First-order decay of [O] in the O+NF₂ reaction. Typical data are shown for $[O]_0 = 1.5 \times 10^{12} \text{ cm}^{-3}$; pseudo first-order conditions with $[NF_2]_0/[O]_0 \ge 1$. $[NF_2]_0/10^{12} \text{ cm}^{-3}$ as follows: \bigtriangledown , 5.6; \circlearrowright , 17.9; \blacksquare , 27.9; \bigcirc , 44.3.

$N+NF_2$ reaction

In addition, resonance absorption at 120.0 nm was used to determine k_8 , for the N+NF₂ reaction :

$$N + NF_2 \xrightarrow{\kappa_B} 2NF.$$
 (8)

It was believed originally that resonance fluorescence studies of N ${}^{4}S$ atom reactions would not be feasible, because of poor spectrometer transmission in the far vacuum ultraviolet and the short range of proportional dependence of $I_{\rm F}$ upon [N ${}^{4}S$]. However, Cheah and Clyne 30 have successfully developed resonance fluorescence for the determination of k_{8} and of the rate constant for the reaction N ${}^{4}S$ +NO \rightarrow N₂+O, giving a rate constant $k^{298} = (3.4\pm0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, in good agreement with the literature on the N+NO reaction. The value of k_{8} for the N+NF₂ reaction, 30 namely $(4.7\pm0.3) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K, therefore should be reliable.

The resonance absorption data on k_8 were obtained using pseudo first-order conditions, with $[NF_2]_0$ in the range 5.2×10^{12} to 2.6×10^{13} cm⁻³. $[N]_0$ was varied in the range $0.95-1.77 \times 10^{12}$ cm⁻³; thus, a typical value of $[NF_2]_0/[N]_0$ was 15. The unresolved ${}^{4}P_{J}{}^{-4}S$ triplet of N near 120 nm was used, ¹⁶ together with the consensus f_{ik} value ¹⁶ and $\alpha = 1.8$.

NF_2 radical reactions

| | | | | k_{5}^{app} |
|---------|------------------------------------|--|--------------------|---|
| run no. | $[NF_2]_0/10^{13} \text{ cm}^{-3}$ | [NF ₂] ₀ /[O] ₀ ^a | k'/s ⁻¹ | $/10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ |
| 1 | 1.20 | 8.0 | 55 | 4.6 |
| 2 | 1.62 | 10.8 | 67 | 4.2 |
| 3 | 1.36 | 9.1 | 51 | 3.8 |
| 4 | 1.09 | 7.3 | 39 | 3.6 |
| 5 | 0.95 | 6.3 | 25 | 2.7 |
| 6 | 0.81 | 5.4 | 21 | 2.6 |
| 7 | 0.56 | 3.7 | 21 | 3.7 |
| 8 | 1.68 | 11.2 | 48 | 2.9 |
| 9 | 2.12 | 14.1 | 69 | 3.2 |
| 10 | 1.79 | 11.9 | 55 | 3.1 |
| 11 | 2.00 | 13.3 | 61 | 3.1 |
| 12 | 2.36 | 15.7 | 85 | 3.6 |
| 13 | 2.79 | 18.6 | 87 | 3.1 |
| 14 | 3.17 | 21.1 | 94 | 3.0 |
| 15 | 3.08 | 20.5 | 113 | 3.7 |
| 16 | 4.43 | 29.5 | 151 | 3.4 |
| 17 | 4.27 | 28.5 | 136 | 3.2 |
| 18 | 3.77 | 25.1 | 129 | 3.4 |
| 19 | 4.05 | 27.0 | 72 | 1.8 |
| 20 | 4.91 | 32.7 | 88 | 1.8 |
| 21 | 5.66 | 37.7 | 95 | 1.7 |
| 22 | 5.48 | 36.5 | 118 | 2.2 |
| 23 | 6.68 | 44.5 | 104 | 1.6 |
| 24 | 6,76 | 45.1 | 103 | 1.5 |
| 25 | 7.15 | 47.7 | 93 | 1.3 |
| 26 | 7.55 | 50.3 | 162 | 2.2 |
| 27 | 7.85 | 52.3 | 160 | 2.0 |

Table 1.--(a) Rate constant k_5 for the O+NF₂ reaction at 298 K: data summary

^{*a*} [O]₀ = 1.5×10^{12} cm⁻³.

(b) Rate constant k_8 for the $\rm N+NF_2$ reaction at 298 K : data summary

| run no.ª | $[NF_2]_0/10^{13} \text{ cm}^{-3}$ | k'/s ⁻¹ | $k_8/10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ |
|----------|------------------------------------|--------------------|--|
| 1 | 0.70 | 24 | 3.4 |
| 2 | 0.80 | 27 | 3.4 |
| 3 | 0.90 | 30 | 3.3 |
| 4 | 0.90 | 29 | 3.2 |
| 5 | 1.0 | 35 | 3.5 |
| 6 | 1.2 | 50 | 4.2 |
| 7 | 1.3 | 27 | 2.1 |
| 8 | 1.3 | 27 | 2.1 |
| 9 | 1.4 | 41 | 2.9 |
| 10 | 1.5 | 39 | 2.6 |
| 11 | 1.5 | 38 | 2.5 |
| 12 | 1.8 | 57 | 3.1 |
| 13 | 1.8 | 51 | 2.8 |
| 14 | 2.0 | 58 | 2.9 |
| 15 | 2.3 | 63 | 2.7 |
| 16 | 2.5 | 71 | 2.8 |
| 17 | 2.6 | 66 | 2.5 |

^a [N]₀ in the range $(0.95-1.77) \times 10^{12}$ cm⁻³.

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Satisfactory first-order decay plots were obtained, with no evidence for a dependence of pseudo first-order rate constant k' upon [NF₂]. Assuming that the secondary reaction $N + NF \rightarrow N_2 + F$ is not important,²⁰ seventeen independent data gave a value of k_8 equal to $(3.0 \pm 1.2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K. Table 1(b) contains a summary of the data.

REACTION OF N ${}^{4}S$ atoms in the H+NF₂ overall reaction

Although the presence of free nitrogen atoms in the $H+NF_2$ reaction system has been inferred previously,^{5, 6} no direct evidence has been available. In the present work, ground-state N ^{4}S atoms were detected directly, as products of the H+NF₂ reaction system, by monitoring resonance absorption in the N $3s^4P_J - 2p^3 \, ^4S$ multiplet at 120.0 nm. The N atoms were formed in the strongly exoergic secondary reaction (4), which follows the initial step, *i.e.*,

$$H + NF_2 \rightarrow HF + NF \tag{1}$$

$$H + NF \to HF + N. \tag{4}$$

The concentrations of H atoms and of NF_2 radicals necessary to form detectable N ⁴S atoms (> 7×10^{10} cm⁻³) were much greater than those used in the kinetic studies just described. Typical $[H_0]$ was 2.5×10^{13} cm⁻³, with $[NF_2]_0 > 1 \times 10^{13}$ cm⁻³.

(a) (b) 5 0 Ω 5 5 10 0 10 $[NF_2]_0/10^{13} \text{ cm}^{-3}$ (c) (d)FIG. 6.—Formation of N ^{4}S atoms in the H+NF reaction. Curves show variation of [N ^{4}S] with

 $[NF_2]_0$, as a function of increasing reaction time as follows: (a) 5; (b) 8; (c) 12; (d) 15 ms. Broken line is computed fit to data.

Fig. 6 shows data for the formation of N 4S atoms, as a function of added [NF₂]₀, for typical reaction times of 5, 8, 12 and 15 ms. In all these runs, free H atoms were verified to be present in the reaction products by resonance absorption. As shown in fig. 6, the N ^{4}S concentration increased to a nearly constant value as the reaction time was increased. Also, the magnitude of $[N {}^{4}S]$ increased as a function of added $[NF_2]_0$. However, with added $[NF_2]_0$ sufficiently high to completely deplete the H atoms, no significant concentrations of N 4S atoms were found in the reaction products due to reaction of free NF₂ with N ⁴S stoms.



The absolute concentrations of N⁴S atoms were obtained from the fractional absorption in the unresolved triplet at 120.0 nm and a direct calibration on N atoms from a microwave discharge using the N+NO titration. The maximum value of $[N^{4}S]$ produced in the H+NF system was 4.7×10^{11} cm⁻³. All absolute N atom concentrations are estimated to be accurate to ± 15 %, in light of the small absorptions which had to be measured.

CHAIN PROPAGATION IN THE $H+NF_2$ SYSTEM

The work of Clyne and White ^{6, 32} on the overall $H+NF_2$ reaction indicated the existence of an efficient self-propagating chain mechanism involving H, H₂ and NF₂. They reported additionally that mixtures of H₂ and N₂F₄ can be made to react spontaneously in a room-temperature flow system at 5 Torr, giving intense NF and N₂ chemiluminescence.³²

(a) 5^{-1} 5^{-1} 5^{-1} 5^{-1} 10^{-1} 5^{-1} 10^{-1} 5^{-1} 10^{-1} 5^{-1} 10^{-1}

FIG. 7.—H atom profiles in the H+NF₂ chain reaction. (a) low [H₂]₀ and [H]₀. Curve shows experimental data for [H] remaining after 15 ms, as a function of $[NF_2]_0$. [H]₀ = 8×10^{12} cm⁻³; [H₂]₀ $\approx 8 \times 10^{13}$ cm⁻³. (b) high [H₂]₀ and [H]₀. Points are experimental data (15 ms). Broken line is computed profile. [H]₀ = 1.4×10^{13} ; [H₂]₀ $\approx 5 \times 10^{14}$ cm⁻³.

The mechanism for the overall $H+NF_2$ reaction has been investigated in the present work, using Lyman- β resonance absorption to follow the H atom concentration. Only at high reagent concentrations ($[H]_0$ and $[NF_2]_0 > 1 \times 10^{13}$ cm⁻³ and $[H_2]_0 > 1 \times 10^{14}$ cm⁻³) was a chain reaction observed. We infer that NF radicals and F atoms, as well as H atoms, are chain carriers in the overall $H+NF_2$ reaction.

Fig. 7 shows typical data for the H atom concentration remaining after 15 ms from the initiation of the $H+NF_2$ reaction. In fig. 7(*a*), initial concentrations were :

 $[H]_0 = 8 \times 10^{12} \text{ cm}^{-3}$, $[H_2]_0 = 5 \times 10^{13} \text{ cm}^{-3}$ and $0.0 \leq [NF_2]_0 \leq 9.6 \times 10^{13} \text{ cm}^{-3}$. The half-reaction time for reaction (1) is calculated to be 1.3 ms, based on $k_1 = 1.5 \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹ and a mean NF₂ concentration of $5 \times 10^{13} \text{ cm}^{-3}$. Thus, reaction (1) was essentially complete within 15 ms. The data of fig. 7(a) therefore show appreciable regeneration of hydrogen atoms, since some H atoms still remained after 15 ms following the addition of a twelve-fold excess of NF₂ to the initial H atoms.

Fig. 7(b) illustrates the regeneration of H in a more striking fashion. In this case, $[H]_0 = 1.4 \times 10^{13} \text{ cm}^{-3}$, $[H_2]_0 = 5 \times 10^{14} \text{ cm}^{-3}$ and $0.0 \leq [NF_2]_0 \leq 9.6 \times 10^{13} \text{ cm}^{-3}$. Virtually no decrease in [H] was observed after 15 ms, even using the largest concentrations of NF₂ where $[NF_2]_0/[H]_0 = 7.4$. The data of fig. 7(b) show that efficient recycling of H occurs in a chain mechanism whose chain length is ≥ 20 . Comparison with fig. 7(a) clearly indicates that the magnitude of $[H_2]_0$ is important in leading to efficient recycling of H atoms.

In some preliminary kinetic runs on the $H+NF_2$ reaction, where relatively high H and H_2 concentrations were used, the first-order plots of log_{10} [H] against time showed significant intercepts on the ordinate axis (compare, however, data of fig. 3 where no such intercepts were observed). This behaviour can be understood in terms of partial regeneration of H atoms following the initial step.

MASS SPECTROMETRIC STUDIES

Direct evidence for the role of H_2 in the $H+NF_2$ reaction has been obtained in mass spectrometric work by Clyne *et al.*³³ These workers found considerable depletion of H_2 and were able directly to detect free NF radicals in the $H+NF_2$ reaction system, using conditions similar to those of fig. 7(*b*).

DISCUSSION

CHAIN MECHANISM IN THE $H+NF_2$ SYSTEM

The above results show that the initial reaction (1) is followed by rapid secondary steps capable of efficiently recycling H atoms with a chain length ≥ 20 . H₂ and NF were shown to be involved in the mechanism, whilst small concentrations of N atoms were found in the reaction products. For the reasons indicated below, however, N atoms are not believed to play a major role in determining the stoichiometry of the chain reaction. On the other hand, F atoms (which were not monitored directly) clearly participate in the chain mechanism. Reaction (4) is terminating because two radicals (H, NF) are consumed, but only one (N) is formed. The major steps in the chain mechanism are reactions (1), (2) and (9), thus :

$$H + NF_2 \rightarrow HF + NF \tag{1}$$

$$NF + NF \rightarrow N_2 + 2F$$
 (2)

$$F+H_2 \to HF+H. \tag{9}$$

Reaction (8)

$$N + NF_2 \xrightarrow{\kappa_8} NF + NF$$
 (8)

is a suitable step for inclusion in the chain propagation scheme. However, reaction (8) must play only a minor role, since $k_8 = 3 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, which is too small to lead to the rapid chain propagation which was observed in the present work.

EVALUATION OF k_2 AND k_4 . COMPUTER MODELLING OF THE REACTION SCHEME

When the minor reactions [(4), (8) and wall recombination (W) of H atoms] are added to the scheme of the three major reactions (1), (2) and (9), the resulting kinetic equations are favourable for the evaluation of k_2 and k_4 from computer modelling. There are only two unknown rate constants in the scheme, namely k_2 and k_4 . The two observable quantities to be fitted are the concentration profiles of H atoms and of N atoms as functions of $[NF_2]_0$ and time. It was found that the H atom profile is



 $[NF_2]_0/10^{13} \text{ cm}^{-3}$

FIG. 8.—Computed H and N atom profiles in the $H+NF_2$ chain reaction. (i) H atom profiles as a function of $[NF_2]_0$ after 15 ms. Shows variation with rate constant $k_2/10^{-11}$ cm³ molecule⁻¹ s⁻¹ as follows: (a) 3.5; (b) 1.4; (c) 0.7; (d) 0.35; (e) 0.14. (ii) N atom profiles as a function of $[NF_2]_0$ after 15 ms. Shows variation with rate constant $k_4/10^{-13}$ cm³ molecule⁻¹ s⁻¹ as follows: (a) 12.5; (b) 5.0; (c) 2.5; (d) 1.25; (e) 0.5.

mainly determined by the magnitude of k_2 , whilst the N atom profile is mainly determined by the magnitude of k_4 . Consequently, k_2 and k_4 are not strongly coupled together in the modelling and it was possible to obtain well-defined solutions for their magnitudes by fitting to the experimental data. This favourable situation for the H+NF₂ system can be contrasted with the more common cases where unknown rate constants couple strongly together to give the observed concentration profiles. An example of a strongly coupled system is the separation of first-order and second-order rate constants for the decay of OH radicals, when the observed kinetics are of intermediate order.

The set of differential equations specified above for the $H+NF_2$ system were solved by numerical integration employing a step routine.^{31, 34} The usual tests for convergence were employed.^{31, 34} Since the rate constants differed from each other

by one or two orders of magnitude, at most, the integration was particularly straightforward and more elaborate routines designed to solve systems with "stiff" equations were not required.

The input parameters were the initial concentrations $[H]_0$, $[H_2]_0$ and $[NF_2]_0$ and the rate constants k_1 , k_8 , k_9 , k_w . The magnitude of these rate constants were as stated above, with $k_w = 10 \text{ s}^{-1}$ and $k_9 = 2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Values for k_2 and k_4 were varied over a wide range. The best fit to the [H] and [N] profiles was found for $k_2 = 7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_4 = 2.5 \times 10^{-13} \text{ cm}^3 \text{ mole$ $cule}^{-1} \text{ s}^{-1}$. These magnitudes for k_2 and k_4 correctly reproduced the experimental variations of [H] and [N] with $[NF_2]_0$ and with time, as shown in fig. 6(d) and 7.

The results are illustrated by the data of fig. 8, which show the computed variations of [H] and [N] with $[NF_2]_0$ for a reaction time of 15 ms and $[H]_0 = 1.4 \times 10^{13} \text{ cm}^{-3}$. These conditions are typical of those employed in the present experiments; see fig. 6(d) and 7 for comparison. The best-fit computed H atom profile is shown in fig. 6(d), together with the experimental points. In fig. 8(i), the curves (a)-(e) are the computed variations of H atom concentration at 15 ms, as a function of $[NF_2]_0$, using a range of values for k_2 from 3.5×10^{-10} down to 1.4×10^{-11} cm³ molecule⁻¹ s⁻¹. In fig. 8(ii), the curves (a)-(e) show the similar N atom profiles, using a range of values for k_4 from 1.25×10^{-12} down to 5×10^{-14} cm³ molecule⁻¹ s⁻¹. Curve (c) is the best fit curve for the H and N profiles. In fig. 8(i), k_4 has been set equal to 2.5×10^{-13} cm³ molecule⁻¹ s⁻¹.

| | tabulated data are [H]/10 ¹³ cm ⁻³ at $t = 15$ ms $k_4/10^{-13}$ cm ³ molecule ⁻¹ s ⁻¹ | | | | | |
|------------------------------------|--|------|--------------|------|--------------|--|
| $[NF_2]_0/10^{13} \text{ cm}^{-3}$ | 0.5 | 1.25 | 2.5 | 5.0 | 12.5 | |
| 1.4 | 2.33 | 2.32 | 2.29 | 2.25 | 2.13 | |
| 3.6 | 2.24 | 2.22 | 2.19 | 2.13 | 1.96 | |
| 5.5 | 2.18 | 2.15 | 2.11 | 2.05 | 1.87 | |
| 7.8 | 2.08 | 2.06 | 2.02 | 1.97 | 1 .79 | |
| 9.6 | 2.01 | 2.00 | 1 .94 | 1.90 | 1.62 | |

TABLE 2.--(a) H ²S concentration profiles as a function of k_4 *

(b) N ⁴S concentration profiles as a function of k_2^*

| | tabulated data are [N ⁴ S]/10 ¹¹ cm ⁻³ at $t = 15$ ms $k_2/10^{-10}$ cm ³ molecule ⁻¹ s ⁻¹ | | | | |
|------------------------------------|---|--------------|----------------------|--------------|----------------------|
| $[NF_2]_0/10^{13} \text{ cm}^{-3}$ | 0.14 | 0.35 | 0.7 | 1.4 | 3.5 |
| 1.4 | 1.50 | 1.35 | 1.07 | 0.90 | 0.62 |
| 6.5 7.8 | 0.72 0.42 | 0.99 0.75 | 1.12 0.90 0.78 | 1.20 1.10 | 0.83 0.80 0.76 |

* $[H]_0 = 2.5 \times 10^{13} \text{ cm}^{-3}$; $[H_2]_0 = 5.0 \times 10^{14} \text{ cm}^{-3}$ in (a) and (b).

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The results of fig. 8 show that both the H and N atom profiles are sensitive to k_2 and k_4 , respectively.

In the case of the N atom profile [fig. 8(b)], the value of [N] (with $[NF_2]_0 = 1.0 \times 10^{14} \text{ cm}^{-3}$ at t = 15 ms) varies almost linearly with k_4 . However, in the case of the H atom profile [fig. 8(c)], the value of [H] under the same conditions is less sensitive and varies approximately with $\sqrt{k_2}$. Thus, correspondingly greater error limits should be set for k_2 than for k_4 (see below).

Possible coupling of k_2 with k_4 also was investigated. Table 2 shows typical results. Firstly, the dependence of the H atom profile upon k_4 was studied, setting $k_2 = 7.0 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ [table 1(a)]. A two-fold variation in k_4 about the best-fit value of 2.5×10^{-13} cm³ molecule⁻¹ s⁻¹ led to virtually no change in the H atom profile. Secondly, the dependence of the N atom profile upon k_2 was investigated, setting $k_4 = 2.5 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ [table 1(b)]. Again, the N atom profile was little affected by a two-fold variation in k_2 about the best-fit value of 7.0×10^{-11} cm³ molecule⁻¹ s⁻¹. Only with a five-fold reduction in k_2 was a significant change in the N atom profile caused.

In summary, the H atom profile is found to depend mainly on k_2 , whilst the N atom profile depends mainly on k_4 . There is little dependence of [H] upon k_4 and of [N] upon k_2 for a moderate variation (\pm a factor of two) in the rate constants. Considering the experimental errors and the sensitivity of the data to k_2 and k_4 described above, we may estimate error limits (1 σ) for k_2 and k_4 (cm³ molecule⁻¹ s⁻¹) as follows:

$$k_2 = (7.0 \pm 3.5) \times 10^{-11}$$
 and $k_4 = (2.5 \pm 0.5) \times 10^{-13}$.

DECAY KINETICS OF NF RADICALS

The present work indicates that predominant removal of NF radicals occurs by rapid bimolecular disproportionation according to reaction (2),

$$NF + NF \xrightarrow{\kappa_2} N_2 + 2F.$$
 (2)

Similar kinetic behaviour was found for BrO radicals and ClO radicals,³⁴ although in both these cases the rate constants for bimolecular disproportionation are considerably lower than the magnitude of $(7.0\pm3.5)\times10^{-11}$ cm³ molecule⁻¹ s⁻¹ found for k_2 . The rate constants for the disproportionation reactions ClO+ClO, BrO+BrO and BrO+ClO at 298 K are 2.4×10^{-14} , 6.4×10^{-12} and 6.7×10^{-12} , respectively.^{34, 35}

The detailed mechanism of reaction (2) is of interest, but is uncertain. It seems clear that N_2+2F are the sole products of reaction (2), since otherwise the overall $H+NF_2$ chain reaction could not propagate efficiently. The alternative exit channel for NF+NF, to give N+NF₂, seems unlikely to be rapid in view of its probable endoergicity. In fact, it has been reported that N+NF₂ gives F atoms as reaction products;^{5, 36} presumably this occurs in two steps, the first forming NF+NF and the second forming N₂+2F via reaction (2). The point of equilibrium between N+NF₂ and N₂+2F thus lies strongly to the N₂+2F side.

Reaction (2) is unlikely to involve the simultaneous scission of two N—F bonds. More probably, a weakly-bound N—N—F species is formed initially,

$$NF+NF \rightarrow NNF+F$$
.

This NNF species would then collisionally dissociate, to form $N_2 + F$:

$$NNF + M \rightarrow N_2 + F.$$

A mechanism of this type is closely analogous to that found for the ClO+ClO disproportionation reaction, which gives ClOO radicals as an intermediate:^{37, 38}

 $ClO + ClO \rightarrow Cl + ClOO$, $ClOO + M \rightarrow Cl + O_2$.

CONCLUSIONS

The rate constants for the primary reactions of H, O and N atoms with NF₂ radicals have been determined directly for the first time. The $H+NF_2$ reaction forms NF radicals, which decay predominantly *via* a rapid second-order disproportionation reaction (2), giving free fluorine atoms: $NF+NF \rightarrow N_2+2F$. In the presence of H₂, the fluorine atoms regenerate hydrogen atoms, thus propagating a chain mechanism. Free nitrogen atoms, N⁴S, are formed by the relatively slow reaction, $H+NF \rightarrow HF+N$.

In this study, no distinction has been made between ground and excited NF radicals; the conclusions stated here apply to the sum of the concentrations of all electronic states of NF which are present in the reactive system. Excited NF $a^1\Delta$ is the initially-formed state,¹¹ but NF $X^3\Sigma^-$ ground-state NF radicals are produced by quenching of NF $a^1\Delta$; this process is fast using the relatively high molecular concentrations used in the study of the H+NF₂ chain reaction. Although nitrogen atoms were detected explicitly in the ground state, this does not preclude the participation also of excited nitrogen atoms in the reaction system. In fact, we found that, at short reaction times, excited N²D atoms predominate over N⁴S atoms as products of the H+NF₂ reaction sequence; this work will be described in part 2.¹¹

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