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Kinetics of the Reaction of Trifluoromethyl Radicals with Nitrogen-Containing Compounds

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A gas-phase kinetic study of hydrogen abstraction from ammonia, methylamine, dimethylamine and trimethylamine has been carried out in a static system by gas chromatography. The photolysis of trifluoromethyl iodide has been used as source of trifluoromethyl radicals. Arrhenius parameters based on Ayscough's value of $10^{13.36}$ cm^3 mol^{-1} s^{-1} for the recombination of trifluoromethyl radicals have been found. The reactions scheme of trifluoromethyl iodide photolysis in the presence of ammonia and amines has been proposed and kinetically interpreted. The trends in chemical reactivity of CF_3 are discussed and interpreted by enthalpy effects.

Key words: trifluoromethyl iodide, ammonia, amine, hydrogen abstraction, radical reactions, kinetics

The abstraction reactions by free radicals have been extensively studied [1], being important in the atmospheric chemistry. Particularly, CF_3 radicals are atmospherically significant. The depletion of stratospheric ozone by chlorofluorocarbons has motivated the development of alternative compounds that are less toxic. Chlorofluorocarbons have been replaced by more acceptable alternative, like hydrofluorocarbons (HCFs), which are not a serious threat of the ozone depletion [2–4]. However, a full evaluation of the impact of the HFCs in atmosphere is still lacking. The details of the degradation processes, in particular of compounds formed during the atmospheric oxidation of HFCs, are still unknown. One of the main products released in the decomposition of the HCFs is the CF_3 radical [5,6]. The role of CF_3 radicals in stratospheric chemistry has been the subject of several studies [7,8]. In last years the works concerning CF_3 radical reactions with nitrogen-containing compounds have been concentrated on reactions with NO_x [9–12]. It is known that ammonia and amines are emitted into the troposphere mainly from biogenic sources. Therefore, in our laboratory kinetic studies of the reactions of CF_3 radicals with amines and ammonia were undertaken. The present reactions were investigated to gain information on the chemical reactivity of trifluoromethyl radicals towards the compounds discussed.

EXPERIMENTAL

Materials. Trifluoromethyl iodide (Aldrich Chemical Company) was bulb to bulb distilled, degassed and stored in a blackened (in order to prevent incidental photolysis of the compounds) vessel. Ammonia (Nitrogen Company Pulawy), methylamine, dimethylamine, trimethylamine (Aldrich Chemical Company) were purified by low temperature distillation in a stream of dry nitrogen and were stored in a vessel with a greaseless tap. Hexafluoroethane (Fluorochem) and trifluoromethane (Matheson Gas Products) were thoroughly degassed and used for gas chromatograph calibration. The purity of all materials was checked by gas chromatography. No impurities were observed.

Apparatus and procedure. Photolysis experiments were carried out in a quartz reaction vessel of 188.8 cm^3 illuminated volume. The light source was a 125 W medium pressure mercury lamp. In all cases there was no decomposition of nitrogen-containing compounds when they underwent photolysis alone. No dark reaction occurred when a mixture of ammonia or amines with trifluoromethyl iodide was heated over the temperature range used.

The possible products of abstraction reactions, hexafluoroethane and trifluoromethane, were analyzed by gas chromatography on a 3 m column of 100–120 mesh activated alumina at 298 K. The calibration relationships of peak areas against micromole of gas, for C_2F_6 and CF_3H were linear in each case.

RESULTS AND DISCUSSION

Trifluoromethyl iodide was used as a source of trifluoromethyl radicals [13,14] according to

$$CF_3I \rightarrow CF_3 + I \tag{1}$$

In the presence of RH (ammonia, methylamine, dimethylamine, trimethylamine) CF_3H and C_2F_6 are the main products of the trifluoromethyl iodide photolysis. CF_3H is produced mostly in the abstraction reaction

$$CF_3 + RH \rightarrow CF_3H + R \tag{2}$$

On the other hand, the C_2F_6 formation can be ascribed to

$$CF_3 + CF_3 \rightarrow C_2F_6 \tag{3}$$

It can be added that the most likely fate of the R radical formed in (2) is its combination with a CF_3 radical or its dimerization. However, the presence of the resulting compounds in the reaction products could not be verified, because they could have been absorbed on the alumina column. Assuming that CF_3H and C_2F_6 are produced only in (2) and (3) the ratio of rate constants $k_{CF_3H}/k^{1/2}_{C_2F_6}$ can be described by:

$$k_{CF_3H}/k^{1/2}_{C_2F_6} = R_{CF_3H}/R^{1/2}_{C_2F_6}\,[RH] \tag{4}$$

where R_{CF_3H} and $R_{C_2F_6}$ are the rates of formation of CF_3H and C_2F_6 respectively, and [RH] is the initial concentration of ammonia or amines. This equation (4) applied for steady state illumination and for constant formation of the product was tested at 415 K at different NH_3 pressures, at 387 K at different CH_3NH_2 pressures and at 370 K at different $(CH_3)_2NH$ pressures. The ratio of rate constants $k_{CF_3H}/k^{1/2}_{C_2F_6}$ are independent on the initial concentration of ammonia or amines. It is thus concluded that the simple mechanism and the resultant rate equation (4) adequately account for the formation of CF_3H and C_2F_6.

The reaction was studied in the temperatures ranging from 320 K to 516 K using variable pressures of trifluoromethyl iodide, ammonia and three different amines.

The Arrhenius parameters of the hydrogen abstraction reactions of different RH substrates (ammonia, methylamine, dimethylamine, trimethylamine) by trifluoromethyl radicals were evaluated from the dependence of log $(k_{CF_3H}/k^{1/2}_{C_2F_6})$ on the reciprocal of temperature using the least-square method. The errors of the Arrhenius parameters are standard deviations of the least-square fitting procedure and they were evaluated without taking into account the experimental errors. The absolute value of Arrhenius parameters, summarized in Table 1, were calculated using the following recombination rate constant for trifluoromethyl radicals $k_{C_2F_6} = 10^{13.36}$ cm^3 mol^{-1} s^{-1} [15].

Table 1. Arrhenius parameters for hydrogen abstraction reaction from nitrogen-containing compounds by trifluoromethyl radicals.

Compound	Temperature ΔT [K]	E [kJ mol^{-1}]	log A [cm^3 mol^{-1} s^{-1}]	log $k_{400\,K}$ [cm^3 mol^{-1} s^{-1}]	ΔH^0 [kJ mol^{-1}]
NH_3	386–516	30.00 ± 0.04	10.00 ± 0.10	6.08	–4
CH_3NH_2	328–456	20.00 ± 0.02	11.49 ± 0.06	8.88	–59
$(CH_3)_2NH$	320–458	18.34 ± 0.02	11.34 ± 0.05	8.97	–84
$(CH_3)_3N$	321–461	16.62 ± 0.04	11.28 ± 0.09	9.11	–111

The data in Table 1 show that the A factors for the CF_3 reactions with amines fall within the range of "normal" values for this type of bimolecular radical reaction. The abstraction reactions of hydrogen atoms from amines are highly exothermic (see Table 1). The values of the rate constant k_{400K}, also listed in Table 1, show the trend of relative reactivity of CF_3 radicals to the studied compounds. The rate constant at 400 K slightly increase with a number of CH_3– (hydrogen atoms) groups in molecule.

It should be underlined that the relative reactivity expressed by the $k_{400\,K}$ values given in Table 2 depends predominantly on the activation energy changes related to the RH reagent used. Pre-exponential factor of the Arrhenius equation does not depend strongly on the type of amines used. The activation energies obtained in the present work suggest that a simple dependence exits between the enthalpy of reaction ΔH^0 and the activation energy E. Namely, the activation energy decreases for more exothermic reactions (see Table 1). The enthalpy change ΔH^0 is related to the energy difference of the bonds, which were formed and broken in the abstraction reaction. The following dissociation energies: $D(CF_3–H) = 444$ kJ mol^{-1}, $D(CH_3NH–H) = 385$

kJ mol^{-1}, D($(CH_3)_2N$–H) = 360 kJ mol^{-1}, D($((CH_3)_2NCH_2$–H) = 330 kJ mol^{-1} [16], D(NH_2–H) = 440 kJ mol^{-1}[17] were used for the ΔH^0 calculations.

Hydrogen atom abstraction may occur from both the C–H and N–H bond in methylamine and dimethylamine. Although significant differences in the enthalpy changes calculated for different amines are found (Table 1), the differences in the activation energies are low for the reagents studied. On the other hand, enthalpy of radicals formation are: CH_3NH^* = 184.4 kJ mol^{-1}and $CH_2^*NH_2$ = 140.2 kJ mol^{-1} [18]. It may be concluded that the hydrogen abstraction occurs from CH_3 group of methylamine and dimethylamine rather than from the amino group in its reaction with CF_3 radicals.

The rate constants at 400 K are in the ratio 1:1.23:1.70 for the methylamine, dimethylamine and trimethylamine series, respectively. There exist small differences in the reactivity of trifluoromethyl radicals in relation to amines. The trend of relative reactivity of trifluoromethyl radicals towards the compounds studied origins from the slight differences in the activation energy. It is clear that the enthalpy effect is dominant in the kinetic of hydrogen abstraction reactions under study. From the above discussion it can be concluded that amino groups have very little influence on the hydrogen abstraction reaction by CF_3 radicals from amines. It should be noted that according to [19,20] the analogous reactions of hydrogen abstraction by CF_3 radicals showed the same reactivity direction as in the i.e. present work, that is the rate constants increase from the methylamine to trimethylamine. However, a lower activation energy, and in consequence higher reactions rate and a lower differences in the relative reactivity of trifluoromethyl radicals to the three different amines were found.

The hydrogen abstraction by trifluoromethyl radicals from ammonia have been studied [21–24]. There were some dispute of its Arrhenius parameters. The investigations were repeated to complete kinetic parameters in our experimental conditions in order to compare the reactivity of trifluoromethyl radicals towards ammonia and amines. The Arrhenius parameters for the reaction of CF_3 radicals with NH_3 obtained in the present work are in agreement with those in [23]. In their studies, CF_3 radicals were produced by photolysis of CF_3Cl. It was observed that the using of the different compounds as source of radicals has no influence on the chemical reactivity of the radicals discussed.

Table 2. The comparison of kinetic parameters for CF_3 radicals reactions with ammonia and amines.

Amine	E_{NH_3}–E_{Amine} [kJ mol^{-1}]	A_{NH_3}/A_{Amine}	k_{NH_3}/ k_{Amine}
CH_3NH_2	10.00	1:31	1:631
$(CH_3)_2NH$	11.66	1:23	1:776
$(CH_3)_3N$	13.38	1:19	1:1072

Table 2 shows big differences in the Arrhenius parameters for the hydrogen abstraction from ammonia and amines. At 400 K, CF_3 radicals attack on methylamine, dimethylamine and trimethylamine is faster than on ammonia by a factor 631, 776 and 1072, respectively. This is mainly due to the lowering in activation energy $E_{NH_3} > E_{Amine}$. The hydrogen atom attached to the carbon atom is more reactive than the corresponding hydrogen atom attached to the nitrogen atom. The differences in reactivity reflect the differences in bond dissociation energies of N–H bond in ammonia and of C–H bond in amines.

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REFERENCES

1. Kerr J.A. and Moss S.J. (Eds.): Handbook of Bimolecular and Thermomolecular Gas Reactions, CRS Press, Bocca Raton 1981.
2. Farman J.D., Gardiner B.G. and Shanklin J.D., *Nature*, **315**, 207 (1985).
3. Solomon S., *Nature*, **347**, 6291 (1990).
4. Wallington T.J., Schneider W.F., Sehested J. and Nielsen O.J., *Disc. Farad. Soc.*, **100**, 55 (1996).
5. Wallington T.J., Schneider W.F., Worsnop D.R., Nielsen O.J., Sehested J., Debruyn W.J. and Shorter J.A., *Environ. Sci. Technol.*, **28**, 320A (1994).
6. Nielsen O.J., Gamborg E., Sehested J., Wallington T.J. and Hurly M.D., *J. Phys. Chem.,* **98**, 9518 (1994).
7. Caralp F., Lesclaux R. and Dognon A.M., *Chem. Phys. Lett.*, **129**, 433 (1986).
8. Clemitshaw R.C. and Sodeau J.R., *J. Phys. Chem.,* **93**, 3552 (1986).
9. Wallington T.J., Dagaut P. and Kurylo M.J.*, J. Chem. Rev.*, **92**, 667 (1992).
10. Bevilacqua T.J., Hanson D.R. and Howard C.J.*, J. Phys. Chem.,* **97**, 3750 (1993).
11. Turnipssed A.A., Barone S.B. and Ravishankara A.R.*, J. Phys. Chem.,* **98**, 4594 (1994).
12. Pagsberg P., Jodkowski J.T., Ratajczak E. and Sillesen A., *Chem. Phys. Lett.,* **286**, 138 (1998).
13. Dacey J.R., *Disc. Farad. Soc.*, **14**, 84 (1953).
14. Clemitshaw K.C. and Sodeau J.R., *J .Photochem. Photobiol. A: Chem.*, **86**, 9 (1995).
15. Aycough P.B.*, J. Chem. Phys.,* **24**, 944 (1956).
16. Kerr J.A., *Chem. Rev.*, **66**, 465 (1966).
17. Demissy M. and Lesclaux R.J., *J. Am. Chem. Soc.*, **102**, 2897 (1980).
18. Benson S.W., Cruickshank F.R., Golden D.M., Huagen G.R., O'Neal H.E., Rodgers A.S., Shaw R. and Walsh R., *Chem. Rev.*, **69**, 279 (1969).
19. Morris E.R. and Thynne J.C.J., *Trans. Farad. Soc.*, **64**, 2124 (1968).
20. Morris E.R. and Thynne J.C.J., *Trans. Farad. Soc.*, **64**, 3021 (1968).
21. Gray P., Arthur N.L. and Lloyd A.C., *Trans. Farad. Soc.*, **65**, 775 (1969).
22. Lefeve H.F. and Timmons R.B., *J. Phys. Chem.,* **73**, 3854 (1969).
23. Fagarash M. B. and Moin F.B., *Kinet. Katal.,* **9**, 1377 (1968).
24. Morris E.R. and Thynne J.C.J., *Int. J. Chem. Kinet.,* **2**, 257 (1970).