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Thermal electron attachment to C_6F_5X and C_6H_5X (X=I, Br, Cl, and F)

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Rate constants have been measured for thermal electron attachment to C_6F_5X (X=I, Br, Cl, F, and H) and C_6H_5X (X=I, Br, Cl, and F) at room temperature in N_2 buffer gas (1–100 Torr) using the pulse-radiolysis microwave cavity method. For all the compounds studied, the rate constants are of the two-body type. Unexpectedly, the values for C_6F_5X except C_6F_5H are all the same ($\sim 2\times 10^{-7}$ cm^3 $molecule^{-1}$ s^{-1}), which are higher than most of the previous values, while that for C_6F_5H, measured in Xe and Ar buffer gases, is very low (7×10^{-12} cm^3 $molecule^{-1}$ s^{-1}). For C_6H_5X, the value decreases dramatically with varying X from I to Br to Cl as 1.0×10^{-8} to 6.5×10^{-12} to 3×10^{-14} cm^3 $molecule^{-1}$ s^{-1}, and that for C_6H_5F must be much lower than 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. These results for the magnitude of the rate constant are rationalized by the variation in the energy of a transient negative-ion state of each molecule, which results from a combination of the electron affinities of constituents (halogen atom X and C_6F_5 radical) and the strength of the C_6F_5–X (or C_6H_5–X) bond.

I. INTRODUCTION

The rate of electron attachment to molecules in the gas phase depends strongly on the structure of the electron-attaching molecule. As shown in many halocarbons,[1] halogen atoms, despite their similarity in electron affinity, often result in considerable differences in the electron-attachment rates when they are substituted into molecules. In this respect, the electron attachment to monohalogenated benzenes C_6H_5X (X is a halogen atom) and halopentafluorobenzenes C_6F_5X are interesting. The species of negative ions formed from low-energy electron attachment to these molecules are well established, i.e., C_6H_5Cl, C_6H_5Br, and C_6H_5I capture electrons dissociatively to give Cl^-, Br^-, and I^- ions, respectively,[2] while the electron attachment to C_6F_5X produces $C_6F_5X^-$, X^-, $C_6F_5^-$, and other ions with different yields depending on the halogen atom X (Refs. 3 and 4) and the experimental conditions such as measurements in a bulk system,[3] electron collisions at low pressures,[4,5] or the electron transfer by atom–beam impact.[6,7] On the contrary, data of rate constants for electron attachment to these compounds are very scarce. Only hexafluorobenzene C_6F_6 has been studied extensively by many workers[8–14] and has attracted much attention recently because of its unusual negative-temperature dependence of the rate constant.[11,12] It seems, however, that even the rate constant at room temperature for this compound has not been settled yet, as there is a discrepancy of more than twice in the magnitude among the published data. For C_6F_5X (X=I, Br, and Cl), one can find very limited data in the literature[3] and no previous data are available for C_6H_5X (X=I, Br, Cl, and F).

In this paper, we report the rate constants for thermal electron attachment to C_6H_5X's and C_6F_5X's measured with the pulse-radiolysis microwave-cavity (PRMC) method which we believe gives accurate values for thermal electrons. Based on the obtained rate constants, the effects of the nature of a halogen atom and the molecular structure on the attachment rates are discussed.

II. EXPERIMENT

The PRMC method was used to measure lifetimes of thermal electrons that decay by attachment to halogenated compounds. Each compound was mixed with nitrogen employed as a buffer gas. The details of the method and the apparatus were described elsewhere.[15] Briefly, a gas sample in the cavity at the end of the x-band microwave circuit was irradiated by a 3 ns x-ray pulse from a Febetron 706, and the output from detectors in the circuit, which is proportional to a shift of the resonant frequency of the cavity, was amplified and fed to a digital oscilloscope. For some compounds, it was experimentally convenient to perform measurements using an experimental setup employed for other electron attachment studies with microwave-heating technique.[16,17] The difference was to use the two-way mode cavity and to employ Ar or Xe as the buffer gas in order to increase the detection sensitivity.

The gas pressures were measured with "Baratron" capacitance manometers (type 220 B-100 and 222 B-1). Most experiments were performed using N_2 as the buffer gas which was of >99.999% purity (supplied by Nihon Sanso). The compounds investigated and their purities are as follows: C_6F_6 (>99%), C_6H_5Cl (>99%), C_6H_5Br (>98%), and C_6H_5I (>97%) supplied by Wako Chemicals; C_6H_5F (>99%) and C_6F_5Cl (>95%) by Tokyo Kasei Kogyo; C_6F_5Br (99%), C_6F_5I (99%), and C_6F_5H (99%) by Aldrich. Samples of C_6F_6 (>99.9%) and C_6F_5Cl (>99%) supplied by Aldrich and of C_6H_5I by Tokyo Kasei were also used for comparison. They were used after degasing at 77 K. All the measurements were carried out at room temperature (298±3 K).

The data have been analyzed in terms of an effective two-body attachment rate constant k_{eff} for an apparent reaction $e^- + AX \rightarrow$ negative ions, where AX denotes an electron-attaching compound. The rate constant is obtained from the disappearance of the electron signal with time.

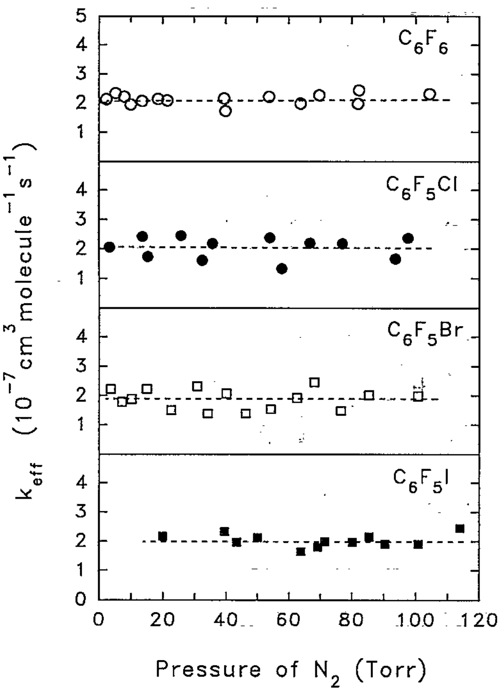

FIG. 1. The dependence on N_2 pressure of the effective two-body rate constant k_{eff} for thermal electron attachment in C_6F_5X–N_2 mixtures at room temperature (~298 K). C_6F_5X (in percent) ($\times 10^{-5}$)—2.9–3.2 (X=F); 4.1–5.2 (X=Cl); 2.8 (X=Br); 4.6–6.2 (X=I).

III. RESULTS AND DISCUSSION

A. C_6F_5X

Shown in Fig. 1 is the dependence of the effective rate constant k_{eff} for thermal electron attachment to C_6F_5X (X=F, Cl, Br, and I) on N_2 pressure. Apparently, the values are constant over a wide range of N_2 pressure and therefore the attachment reaction is of the two-body type for these compounds. From these results, we obtain the two-body rate constants of $(2.1\pm0.3)\times10^{-7}$, $(2.0\pm0.5)\times10^{-7}$, $(1.9\pm0.4)\times10^{-7}$, and $(2.0\pm0.3)\times10^{-7}$ cm^3 molecule^{-1} s^{-1} for X=F, Cl, Br, and I, respectively. A general reaction scheme for the negative ion production from low-energy electron capture by C_6F_5X can be written simply as

$$e^- + C_6F_5X \rightarrow C_6F_5X^{-*} \rightarrow C_6F_5X^-,\ X^-,\ C_6F_5^-. \quad (1)$$

The electron affinities of halogen atoms [3.399 eV (F), 3.617 eV (Cl), 3.365 eV (Br), and 3.059 eV (I)] (Ref. 18) and C_6F_5 ($\geqslant$3.4 eV) (Ref. 5) and the bond-dissociation energies for C_6F_5–X [4.94 eV (F) (Ref. 18), 3.99 eV (Cl) (Ref. 18), 3.5 eV (Br) (Ref. 19), and 2.87 eV (I) (Ref. 18)] show that for C_6F_6 and C_6F_5Cl, the dissociative attachment of zero-energy electrons is highly endothermic for the three channels represented by scheme (1). For C_6F_5Br, both the production of Br^- and that of $C_6F_5^-$ are only 0.1 eV endothermic, while for C_6F_5I, the I^- formation and the $C_6F_5^-$ production are exothermic by 0.18 and 0.5 eV, respectively. The relative yields for each negative ion measured by Herd *et al.*[3] for thermal electron attachment in a bulk system are in accord with these energetics, i.e., $C_6F_5Cl \rightarrow C_6F_5Cl^-$ (100%), $C_6F_5Br \rightarrow C_6F_5Br^-$ ($\geqslant$97%)+Br^- ($\leqslant$3%), and $C_6F_5I \rightarrow C_6F_5^-$ ($\geqslant$95%)+$C_6F_5I^-$ ($\leqslant$5%). In C_6F_6, only its parent negative ion can be formed in the low-energy electron attachment.[4,5] Although the electron affinities of C_6F_5X's are not known except C_6F_6 [the most recent value=0.52±0.1 eV (Ref. 19)], positive values are reasonable for all C_6F_5X. The two-body nature observed here suggests that the lifetimes of transient negative ions $C_6F_6^{-*}$, $C_6F_5Cl^{-*}$, and $C_6F_5Br^{-*}$ are long enough to allow collisional stabilization by N_2 molecules. This is consistent with results by Naff *et al.*[4] who have measured, using the time-of-flight (TOF) mass spectrometer, the lifetimes of the $C_6F_5X^{-*}$ ions to be 12.0, 17.6, and 20.8 μs for X=F, Cl, and Br, respectively. For C_6F_5I, the dissociation channel of the parent negative ion into $C_6F_5^-$+I must be faster than the collisional stabilization rate.

Rate constants obtained for thermal electron attachment are summarized in Table I. It is quite surprising that all of the rate constants for C_6F_5X (X=F, Cl, Br, and I) are the same (~2×10^{-7} cm^3 molecule^{-1} s^{-1}). We should

TABLE I. Thermal electron attachment rate constants k_{eff} (in units of cm^3 molecule^{-1} s^{-1}) at room temperature (~298 K) for C_6F_5X (X=F, Cl, Br, I, and H).

C_6F_6		C_6F_5Cl		C_6F_5Br		C_6F_5I		C_6F_5H	
$k_{eff}\times10^7$	Ref.	$k_{eff}\times10^7$	Ref.	$k_{eff}\times10^7$	Ref.	$k_{eff}\times10^7$	Ref.	$k_{eff}\times10^{12}$	Ref.
2.1±0.3	a	2.0±0.5	b	1.9±0.4	b	2.0±0.3	b	7±2	c
2	14	0.84	3	0.83	3	0.31	3	<100	12
1.5	11							100	14
1.1	12								
1.06	8								
1.02	9								
~1	7								
0.30	10								

[a] Present work, with N_2, Ar, and Xe buffer gases.
[b] Present work, with N_2 buffer gas.
[c] Present work, with Ar and Xe buffer gases.

note that use of C_6F_6 and C_6F_5Cl from different manufacturers gave the same results. There are several literature values for C_6F_6. The present value for C_6F_6 is in good agreement with that measured by the pulse sampling method,[14] but somewhat higher than other previous values obtained by swarm methods[8,9,11] and a flowing afterglow Langmuir probe (FALP) procedure.[12] The values measured by using high-Rydberg atom beams[7,10] are lower than other values. In contrast to C_6F_6, there are few previous data for compounds with X=Cl, Br, and I. It is seen from Table I that the present values for C_6F_5Cl, C_6F_5Br, and C_6F_5I are more than two times higher than those obtained by Herd *et al.*[3] using the FALP method, and the discrepancy is quite severe for C_6F_5I. C_6F_6 is known to show a dramatic decrease in the attachment rate constant with increasing temperature[11,12] and the value also decreases with increasing electron energy.[11] The decrease of the rate constant with temperature has been interpreted by the increase in the rate of electron detachment from the parent negative ion $C_6F_6^-$ with increasing temperature.[20,21] Thus, any unexpected increase in gas temperature or electron energy may cause a drop in the measured thermal electron attachment rate constant. The effects of gas temperature, however, cannot be responsible for the discrepancies found in C_6F_5X (X=Cl, Br, and I), since the FALP study has also shown that when the gas temperature increases from 300 to 450 K, the rate constants increase from 8.4×10^{-8} to 1.3×10^{-7} cm^3 molecule^{-1} s^{-1} for C_6F_5Cl, from 8.3×10^{-8} to 2.4×10^{-7} cm^3 molecule^{-1} s^{-1} for C_6F_5Br, and from 3.1×10^{-8} to 1.2×10^{-7} cm^3 molecule^{-1} s^{-1} for C_6F_5I. The gas temperature in the present study is strictly at room temperature (298 K) and no excess heating by applied microwaves can be expected. Therefore unless the gas temperature in the FALP study is significantly lower than that stated, which is unlikely though the discrepancy cannot be explained by the difference in the gas temperature.

One can invoke the effect of the electron energy for the reason for the discrepancy. If the electron temperature in the FALP study was higher than the gas temperature for some reason, the measured rate constants could be lower than the true ones. This is based on the assumption that as for C_6F_6 the rate constants for C_6F_5X (X=Cl, Br, and I) decrease sharply with increasing mean electron energy. Indeed there is evidence that these compounds show steep declines of the rate constants when the mean electron energy increases from thermal to 1 eV.[22] In order to check the reliability of our data and to obtain further insight into the effects of electron energy on the measured rate constants, additional measurements have been performed using Ar and Xe as the buffer gas. The experiment has been made with a setup used for studies of electron-energy dependence of electron attachment.[16,17] Measurements using Ar at 200–500 Torr containing C_6F_6 at 9.1×10^{-6} to 1.8×10^{-5} Torr have yielded the rate constant of $(2.1\pm0.4)\times10^{-7}$ cm^3 molecule^{-1} s^{-1}, but those with Ar at 70 Torr containing C_6F_6 at 9.1×10^{-6} to 4.1×10^{-5} Torr have shown lower rate constants ranging from 1.7×10^{-7} to 1.1×10^{-7} cm^3 molecule^{-1} s^{-1}. In 70 Torr Xe buffer gases, it has been found that the rate constant is 2.0×10^{-7} cm^3 molecule^{-1} s^{-1} for mixtures containing 5×10^{-6} Torr C_6F_6, but decreases with the increasing pressure of C_6F_6, i.e., 1.3×10^{-7} cm^3 molecule^{-1} s^{-1} (for 1.4×10^{-5} Torr C_6F_6) and 5.8×10^{-8} cm^3 molecule^{-1} s^{-1} (for 7.4×10^{-5} Torr C_6F_6). Similar results have also been obtained in measurements for C_6F_5Cl and C_6F_5I in 70 Torr Xe; i.e., both compounds give 2×10^{-7} cm^3 molecule^{-1} s^{-1} at their pressures of 5×10^{-6} Torr, but the values become much lower 5.4×10^{-8} cm^3 molecule^{-1} s^{-1} (for 5.5×10^{-5} Torr C_6F_5Cl) and 4.0×10^{-8} cm^3 molecule^{-1} s^{-1} (for 1.1×10^{-4} Torr C_6F_5I). It is apparent that a high pressure buffer gas or a low pressure C_6F_5X must be required to obtain a high rate constant $\sim2\times10^{-7}$ cm^3 molecule^{-1} s^{-1}. Values for C_6F_6 reported previously seem to show this trend. Wentworth *et al.*[14] measured the rate constant under the condition of 1 atm carrier gas (Ar–10% CH_4) and obtained 2×10^{-7} cm^3 molecule^{-1} s^{-1}. Davis *et al.*[8] in their electron swarm measurements in CH_4 or He at pressures below 5 Torr reported 1.06×10^{-7} cm^3 molecule^{-1} s^{-1}. Adams *et al.*[12] obtained 1.1×10^{-7} cm^3 molecule^{-1} s^{-1} using the FALP method which employed He carrier gas at about 1 Torr. The data obtained by using high-Rydberg atom beams[7,10] often show considerably low values at electron energies near thermal, as pointed out in our previous publication.[17] Only electron swarm measurements by Christophorou and colleagues[9,11] employ high-pressure N_2 or Ar (at a few hundred Torr or much higher). The earlier value 1.02×10^{-7} cm^3 molecule^{-1} s^{-1} by Gant and Christophorou[9] could have involved errors because of using an older set of electron energy distribution functions for N_2, as pointed out by Chutjian and Alajajian.[13] Later studies by Spyrou and Christophorou[11] gave a high value 1.5×10^{-7} cm^3 molecule^{-1} s^{-1}, which is obtained by extrapolating their data for the mean electron energies higher than 0.055 eV to thermal energy. All these facts imply the trend described above. The results that low rate constants are obtained at low buffer gas pressures or at high solute pressures can be attributed to the occurrence of the attachment of electrons before their thermalization. In clarifying this effect, it is important to compare the thermalization time of electrons τ_{th} in the buffer gas used and the lifetimes of electrons by attachment to solute molecules. The value of τ_{th} in 70 Torr Ar can be estimated to be about 20 μs on the basis of the data reported by Warman and Sauer.[23] A slightly shorter τ_{th} (about 15 μs) is expected for 70 Torr Xe from the observed microwave conductivity profile.[17] We can easily show that 1×10^{-5} Torr C_6F_6 with the rate constant of 2×10^{-7} cm^3 molecule^{-1} s^{-1} should give an electron lifetime of 15 μs, which is comparable to τ_{th} in 70 Torr Xe or Ar. Thus a C_6F_6 pressure higher than 1×10^{-5} Torr would cause a situation in that electrons must be captured before their thermalization, which then would result in apparently lower rate constants than the true thermal value because the rate constant decreases steeply with increasing electron energy. On the other hand, τ_{th} in N_2 buffer gas is rather short; e.g., about 0.1 μs at 70 Torr. Note that the present measurements using N_2 have been done under the condition that the thermalization time is much shorter than the electron lifetimes and naturally all the resulting data show high rate constants. Then, however, we cannot explain the low rate constants reported by the FALP study, in which electrons produced by discharge of about 1 Torr He flow along a flow tube, and only a very small amount of solute gas, probably on the order of 10^{-7} Torr estimated from another FALP study,[24] is introduced for attachment reaction. Thus the truly thermal condition seems to be satisfied in this case.

The only remaining candidate for the reason for the discrepancy could be the differences in the stabilization efficiency for a transient negative ion $C_6F_5X^{-*}$ between the buffer gas molecules used in the present study and those in the previous studies, especially in the FALP measurements. We usually expect that a high-pressure diatomic or polyatomic gas allows more efficient stabilization than a low-pressure monoatomic (rare) gas. Since, however, the autoionization lifetimes of $C_6F_5X^{-*}$ (X=F, Cl, and Br) are all long ($>10\ \mu$s) at room temperature,[4] we expect that the collisional stabilization is quite effective in most cases studied. Indeed, the Langevin's rate constant for collisions between $C_6F_6^{-*}$ and a buffer gas molecule predicts an average time taken for each collision to be about 10^{-8} s in 1 Torr He (typically used in the FALP studies), and a time shorter than this can be expected for 1 Torr CH_4 (used in the study by Davis *et al.*[8]). If the difference in the stabilization efficiency is the main reason for the discrepancy, one must assume that the stabilization is extremely inefficient in rare gases as well as in methane, but moderately effective in diatomic molecules such as N_2, or polyatomic molecules except methane. Many similar studies of electron attachment suggest that the pressure of 70 Torr of Ar or Xe is sufficiently high for collisional stabilization of transient negative ions with autoionization lifetimes longer than microseconds, yet we have obtained low rate constants when the solute pressure is relatively high. This effect of solute pressure is in contradiction with the usual trend of the efficiency of collisional stabilization. Thus, one might need to propose an unusual nature of the collisional stabilization processes. It is interesting that Davis *et al.*[8] measured rate constants for C_6F_6 in He, CH_4, and C_2H_4 (at 1–5 Torr), and obtained slightly different average values depending on these buffer gases; i.e., 0.942×10^{-7}, 1.00×10^{-7}, and 1.25×10^{-7} for He, CH_4, and C_2H_4, respectively. This order is in accord with that of the stabilization efficiency of buffer gas molecules. Note, however, that the electron thermalization time in these gases also decreases in this order.[23]

In conclusion, the present result that all of the rate constants at thermal electron energy for C_6F_5X (X=F, Cl, Br, and I) are essentially the same ($\sim2\times10^{-7}$ cm^3 molecule^{-1} s^{-1}) is quite reliable. The reason for lower rate constants reported by most previous works might be due to either the observation of attachment of epithermal electrons or the presence of an unusual stabilization property of $C_6F_5X^{-*}$ ions. The former can provide a reasonable explanation for the present results as well as most of previous data except the FALP results. Other experimental and theoretical studies will be needed to clarify these problems.

To obtain insight into the role of the C_6F_5 group in the electron capture process, further measurements have been carried out on C_6F_5H. The experiment was made in the same way as that in the additional measurements for C_6F_6 and both Xe and Ar were used as the buffer gas. It has been found that the two-body rate constant is very low in this case, i.e., $(7\pm2)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} in Xe at pressures between 20 and 80 Torr, and 7.5×10^{-12} cm^3 molecule^{-1} s^{-1} in Ar at 600 Torr. These are much lower than those for halopentafluorobenzenes. Adams *et al.*[12] have reported that the rate constant for C_6F_5H is immeasurably low ($<10^{-10}$ molecule^{-1} s^{-1}), so the present value 7×10^{-12} cm^3 molecule^{-1} s^{-1} is not unreasonable. Fenzlaff and Illenburger[5] have shown that there is no parent-negative-ion production from the low-energy electron attachment to C_6F_5H and that $C_6F_4^-$ and $C_6F_5^-$ are observed with the appearance energies of about 0.7 eV (1.5 eV at the maximum) and 1.5 eV (2.0 eV at the maximum), respectively. C_6F_5X's (X=F, Cl, Br, and I), on the other hand, produce negative ions with the appearance energy of ~0 eV.[4] This difference in the appearance energy, and therefore the resonance energy, should be the main reason for the marked difference in the attachment rate constant between C_6F_5H and C_6F_5X. A high electron affinity of the C_6F_5 radical ($\geqslant$3.4 eV) implies a high efficiency of electron capture for the C_6F_5 group, but the result for C_6F_5H suggests that the C_6F_5 group lowers the energy of the negative ion states considerably, but the effect is not enough to produce stable parent negative ions unless it combines with another halogen atom.

B. C_6H_5X

Results for C_6H_5X (X=Cl, Br, and I) are shown in Fig. 2. The rate constants are of the two-body type and show a marked decrease by orders of magnitude when X varies from I to Br to Cl. In addition to mixtures with N_2, we have carried out measurements for C_6H_5Cl using its pure samples, since the rate constants were so low in this compound that long lifetimes of electron decays observed in N_2 mixtures could involve large errors. The results are included in Fig. 2 using a different symbol and they are consistent with those obtained from N_2 mixtures. We have also made measurements on C_6H_5F. Since for this compound the rate constant was expected to be much lower than that for C_6H_5Cl, the measurement was done again by using pure C_6H_5F samples at pressures below 10 Torr. The rate constants are found to be on the order of 10^{-13} cm^3 molecule^{-1} s^{-1}, but they decrease with irradiation times, i.e., the number of irradiation of x-ray pulses, and inconsistent data have been obtained from measurement to measurement. We have concluded that the difficulty is associated with impurities that possess high electron-attaching ability. The decrease in the rate constant with the increase in the x-ray shot number may be due to the decomposition of the impurities by radiolysis. So the rate constant for C_6H_5F is probably much lower than the order

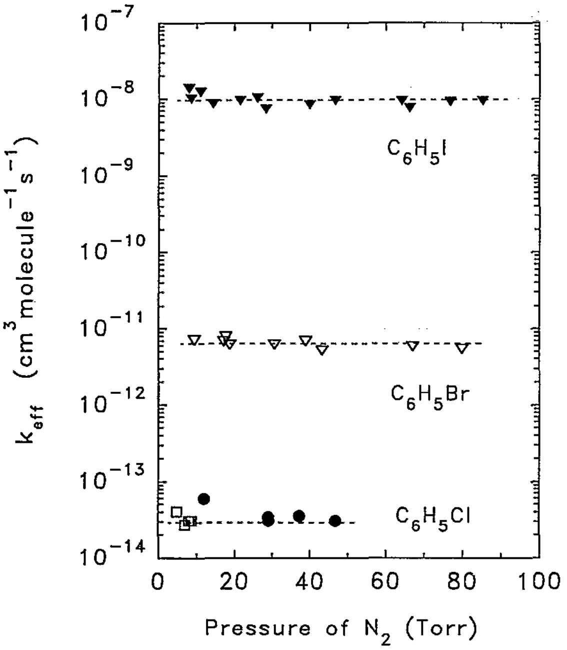

FIG. 2. The dependence on N_2 pressure of the effective two-body rate constant k_{eff} for thermal electron attachment in C_6H_5X–N_2 mixtures at room temperature (~298 K). C_6H_5X (in percent)—3.4–4.1$\times 10^{-4}$ (X=I); 0.77–1.47 (X=Br); 9.85 (X=Cl). In C_6H_5Cl, open squares correspond to pure (100%) samples.

of 10^{-13} cm^3 molecule^{-1} s^{-1}. The values obtained here are listed in Table II. There are no published data available.

Energetically, the dissociative electron attachment to C_6H_5X to produce an X^- ion is endothermic for X=F, Cl, and Br by 2.02, 0.54, and 0.14 eV, respectively,[18] while it is exothermic for X=I by 0.24 eV.[18] On the other hand, the negative-ion resonance maxima have been observed at 1.40, 0.86, 0.84, and ~0 eV for F, Cl, Br, and I, respectively.[2] All these differences result mainly from the differences in the dissociation energy of the bond C_6H_5–X and we can expect the rate constants for thermal electrons being of the order $I > Br > Cl \gg F$. The present results for X=I, Br, and Cl are consistent with this expectation. Since we can expect that the rate constant for C_6H_5F is immeasurably low, the conclusion that the value for this compound in Table II may be due to impurities should be correct. The rate constant for C_6H_5I is 1×10^{-8} cm^3 molecule^{-1} s^{-1}. This value seems to be low considering the exothermicity of the reaction (0.24 eV) and its low resonance energy (~0 eV). Probably the interaction of the C_6H_5 group with electrons is much weaker than that of the C_6F_5 group that acts effectively in the electron capture when it combines with another halogen atom.

TABLE II. Thermal electron attachment rate constants k_{eff} (in units of cm^3 molecule^{-1} s^{-1}) at room temperature (~298 K) for C_6H_5X (X=I, Br, Cl, and F).

C_6H_5I	C_6H_5Br	C_6H_5Cl	C_6H_5F
$(1.0\pm 0.2)\times 10^{-8}$	$(6.5\pm 0.5)\times 10^{-12}$	$(3\pm 1)\times 10^{-14}$	$<10^{-13}$[a]

[a]This value may suffer from effects of impurities.

IV. CONCLUSION

The rates of low-energy electron attachment to monohalogenated benzenes are mostly determined by the halogen atom that is substituted. The main effect of the halogen atom is on the dissociation energy of the C_6H_5–X bond that determines the energy of the dissociation limit and possibly the position of the transient negative ion state as well. As a result, the rate constants for thermal electrons vary several orders of magnitude depending on the halogen atom X. For C_6F_5X, however, the presence of the C_6F_5 group considerably lowers the energy of negative-ion states irrespective of the substituted halogen atom X. This results in high rate constants, essentially the same value of 2×10^{-7} cm^3 molecule^{-1} s^{-1}, for all C_6F_5X.

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