Absolute Rate Constants for Atomic Fluorine in Solution: Characterization of Reaction Intermediates in the Laser Flash Photolysis of Xenon Difluoride

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Abstract: Laser flash photolysis of xenon difluoride in 1,1,2-trichlorotrifluoroethane (Freon-113) yields atomic fluorine, which can be detected via its loose complex with the solvent. This complex, with an absorption maximum at 320 nm, has a lifetime at ambient temperature of about 200 ns and is quenched with rate constants near the diffusion controlled limit by most substrates. In neat hexafluorobenzene as solvent, the heptafluorocyclohexadienyl radical is observed. In addition to the fluorine atom, a second species formed with λ_{max} = 345 nm is assigned to be the XeF radical, with a lifetime of ca. 25 μs in acetonitrile at ambient temperature.

Introduction

The characterization of atomic species as reactive intermediates with the technique of laser flash photolysis, well-developed for atoms in the gas phase, has only recently been applied to atoms in the liquid phase. This is due to difficulties in their detection, as VUV techniques which can be applied in gas-phase studies are no longer feasible in the condensed phase where a potentially absorbing solvent is present in high concentration. Among the atoms studied in solution are the heavy halogen atoms $Cl^\bullet$,[1,2] $Br^\bullet$,[3] and $I^\bullet$,[4] which can be investigated by monitoring charge-transfer complexes with halocarbons, π-complexes with arenes, or the $X_2^{\bullet-}$ anions. The reactivity of hydrogen atoms is well-established from numerous pulse radiolysis studies.[5] The first second-period atom to be characterized in solution was O (^{3}P); it was first studied in water by Kläning et al.,[6] and more recently and extensively by us, using acetonitrile as solvent.[7] The solution reactivity of the oxygen atom is reduced due to the spin-forbidden character of most of its reactions. O (^{3}P) is significantly more selective than hydroxyl. No spin restrictions apply to reactions of the fluorine atom, which is known to be one of the least selective reactive intermediates. Thus the extreme reactivity of $F^\bullet$, combined with the difficulty of finding a suitable photolabile precursor (other than F_2) for it, makes the measurement of solution rate constants for $F^\bullet$ challenging.

The principal criteria to assess the use of a fluorine compound in the photochemical generation of $F^\bullet$ are the X–F bond energy and the UV absorption. Among the molecules with the weakest X–F bonds are the noble gas fluorides; for instance, the first bond dissociation energy of xenon difluoride was determined to be 60.37 kcal/mol.[8] The gas-phase laser flash photolysis of XeF_2 was investigated recently by Bott et al.[9] According to the authors, irradiation of XeF_2 with λ = 193 nm leads to primary cleavage into $F^\bullet$ and XeF, either as the ground state XeF (X) molecule or as the XeF (B) excimer, with a quantum yield of one. As XeF_2 offers the additional advantage of being compatible with a variety of organic substrates for at least a limited time span, we chose it as a promising candidate for a study on the reactivity of $F^\bullet$ in solution.

In this contribution we present evidence for the formation of atomic fluorine upon laser flash photolysis of xenon difluoride in Freon-113. We also report rate constants for the reactions of $F^\bullet$ with a selection of substrates.

Results

The flash photolysis of XeF_2 was investigated in various solvents, using three different laser excitation wavelengths. This section is divided according to the species under study.

Characterization of XeF. Initial experiments were performed in acetonitrile, where λ_{exc} = 266 nm yielded one single transient with a sharp absorption band at λ_{max} = 345 nm and a lifetime of $\tau \sim 25$ μs (Figure 1). Irradiation with the more intense 248 nm pulses from an excimer laser gave rise to a transient with identical absorption characteristics, but in this case the decay was dominated by second-order kinetics. The transient was not affected by purging the solution with oxygen, saturating it with cyclohexane, or adding ca. 5% hydrofluoric acid (48% HF in water); the use of acetonitrile-d_3 also did not alter signal lifetime or intensity. The addition of 0.1% benzene, however, led to a broadening of the transient spectrum with an additional absorption maximum at λ_{max} = 290 nm and probably a very weak band at λ_{max} ~580 nm (Figure 2). In Freon-113 as solvent, the sharp absorption band, slightly red-shifted to λ_{max} = 350 nm, was also observed. We note, however, that irradiation of XeF_2 in Freon-113 with λ_{exc} = 308 nm ([XeF_2] = 6 mM) gave rise only to traces of this transient; we believe that 308 nm excitation results mainly in photolysis of XeF_4, the major impurity (ca. 1%) in commercial xenon difluoride.

The following rationale leads us to assign the 345 nm transient to the ground state XeF radical:

(1) As the transient does not depend on the choice of solvent, it cannot correspond to the primary product of any reaction of fluorine atom with the solvent. It is therefore likely that this transient species still contains xenon.

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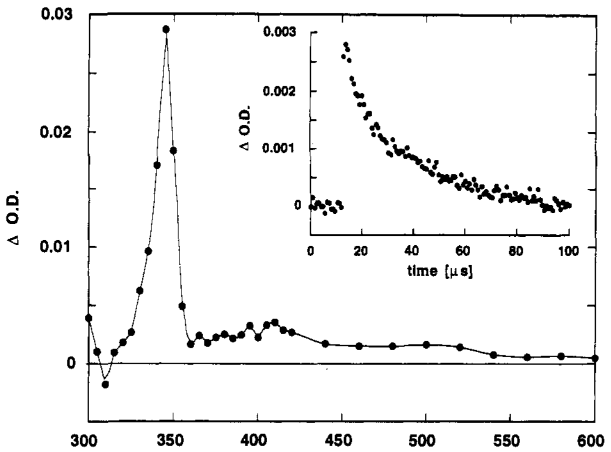

Figure 1. Transient spectrum observed 100 ns after LFP (248 nm) of XeF_2 in CD_3CN under nitrogen. Insert: Decay trace monitored after laser flash photolysis (266 nm) of XeF_2 in CH_3CN under nitrogen.

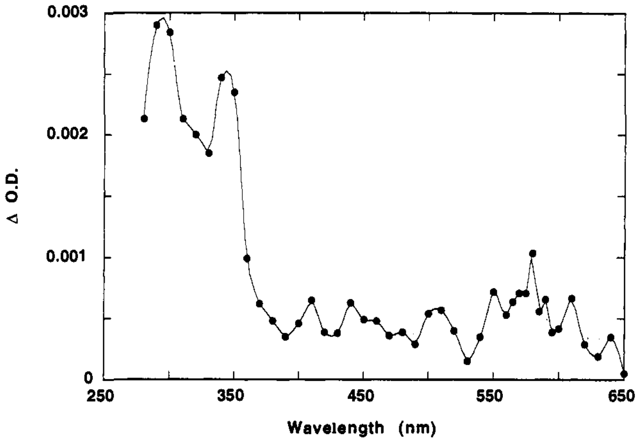

Figure 2. Transient spectrum observed 3 μs after laser flash photolysis (266 nm) ov XeF_2 in CH_3CN containing 0.1% benzene under nitrogen.

(2) From the study conducted by Bott et al.[9] it is clear that the primary decay of excited XeF_2 involves formation of a fluorine atom and of XeF, which in the gas phase—depending on the energy of the light used for excitation—may be formed as excimer (B-state) or in the ground state (X-state), which in turn decays into Xe and F• with a lifetime in the microsecond time scale. While it is conceivable that the 345 nm transient corresponds to the XeF excimer (B-state), we note that a lifetime of 25 μs seems extremely long for an excited state of a free radical in solution living 14 ns in the gas phase. Further, a 204 nm energy threshold was reported for the photochemical formation of XeF (B) from XeF_2 in the gas phase. This is shorter than all the laser sources used in our experiments. Overall, these arguments rule out the formation of the excited intermediate XeF (B).[8]

(3) An absorption maximum at λ = 345 nm for the ground-state XeF (X) molecule in CH_3CN solution agrees well with the known ν_0 of 28773 cm^{-1} (347.5 nm) for the XeF (B-X) system in the gas phase.[8] The ground-state XeF molecule is isoelectronic with the $IF^{\bullet-}$ anion or, if the ionic VB structure Xe^+ F^- is chosen, with the iodine atom. This in turn agrees well with the observed low reactivity of the transient and with the detection of spectral shifts and long-wavelength absorption in the presence of benzene, these features being typical of arene–halogen atom π-complexes.

In acetonitrile solution the XeF radical was the only observable transient. Even on the shortest time scales accessible on our system, no other transient and no growth could be monitored. At room temperature the decay of XeF involves about 75% second order and the rest first order, but at lower temperatures the first order component predominates. We determined the Arrhenius parameters (−42 to +21 °C) for the first order decay as log (A/s^{-1}) = 7.8 and E_a = 2.7 kcal/mol. The error may be rather large as a result of the need to analyze the traces as a mixed first order–second order kinetics. We suggest that the low pre-exponential factor reflects the need for extensive solvent reorganization as a highly polar molecule converts to nonpolar atomic species.

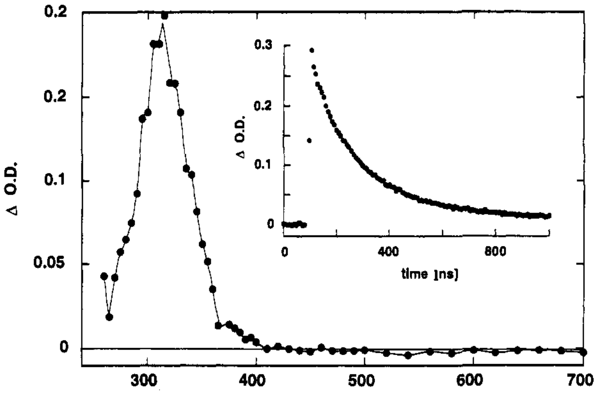

Figure 3. Transient spectrum observed 90 ns after laser flash photolysis (248 nm) of XeF_2 in Freon-113 under nitrogen. Insert: Decay trace monitored after laser flash photolysis (248 nm) of XeF_2 in Freon-113 under nitrogen.

Study of the Reactions of Fluorine Atoms. In degassed Freon-113 laser photolysis of XeF_2 leads to a short-lived species (τ ~ 200 ns) showing first-order decay; the first-order behavior is presumably due to trace impurities in the Freon used. This species has a very intense and broad absorption with λ_{max} = 320 nm and could be detected using 248, 266, or 308 nm excitation (Figure 3). The 320 nm intermediate was completely quenched upon purging the solution with oxygen or adding small amounts of acetonitrile or water. Substituting argon for nitrogen as purge gas did not change its kinetic behavior. A similar transient was observed in $CFCl_3$ (λ_{max} = 310 nm, second-order decay). We attribute the short-lived transients observed to the complexes of the fluorine atom with the respective halocarbon. Complexes of this type have been known for Cl• and CCl_4[2] or Br• and CBr_4 or CH_2Br_2.[10]

A similar transient was also observed in CCl_4 (λ_{max} = 340 nm, first-order decay with a lifetime of ~50 ns). We note that this short lifetime is probably due to trace impurities in the CCl_4 used and does not imply any inherent instability of this complex, since addition of small amounts of CCl_4 to Freon-113 led to an increase in the lifetime of the 320 nm signal as compared to the Freon complex. Given the extreme electrophilicity of the fluorine atom, the observation of complexes between F• and CCl_4 or even the electron-deficient Freon solvents comes as no surprise.

In order to investigate the reactivity of the atomic fluorine/Freon-113 complex, we measured the decay lifetime of the transient at λ = 320 nm against the concentration of various quenchers (Figure 4). The results, as shown in Table 1, clearly reflect the reactivity of the fluorine atom rather than that of a larger molecular complex, as most of the reactions are somewhat faster than the diffusion controlled limit that would be predicted by Debye's formula. As in the case of the oxygen atom,[7] the unusually high diffusion coefficient of the fluorine atom is responsible for the extremely high rates of diffusion controlled reactions. If one assumes neon to be a good model for F•, one can expect that diffusional values for F• should be 2–3 times higher than for O_2, and 5–10 times larger than for typical organic molecules.[11,12,7] Clearly, Debye's formula does not provide an appropriate estimate in these systems.

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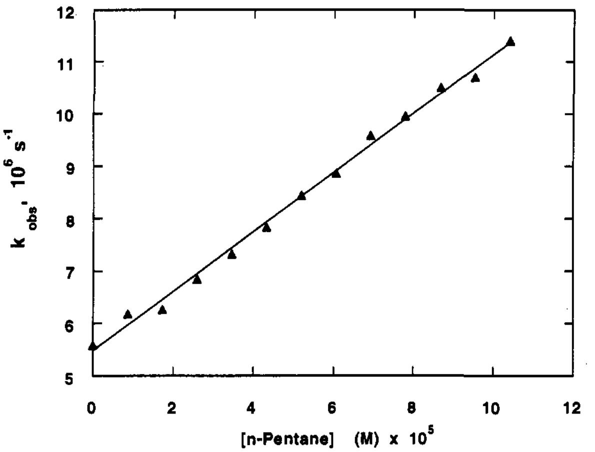

Figure 4. Plot of k_{obs} for the decay of $(F \rightarrow CF_2Cl\text{–}CFCl_2)$, monitored at 320 nm, vs concentration of *n*-pentane added.

Table 1. Rate Constants for the Reaction between the Fluorine Atom and Various Substrates in Freon-113 at Room Temperature[a]

substrate	k, 10^9 M^{-1} s^{-1}
acetonitrile	27
acetonitrile-d_3	16
chloroform	1.8
chloroform-*d*	0.96
oxygen	5.6
hydrogen	5.8
water	40
water-d_2	40
methane	7.0
n-pentane	57
cyclohexane	73
tetrachloroethylene	100
hexafluorobenzene	71

[a] Errors in the rate constants are estimated as 10–15%.

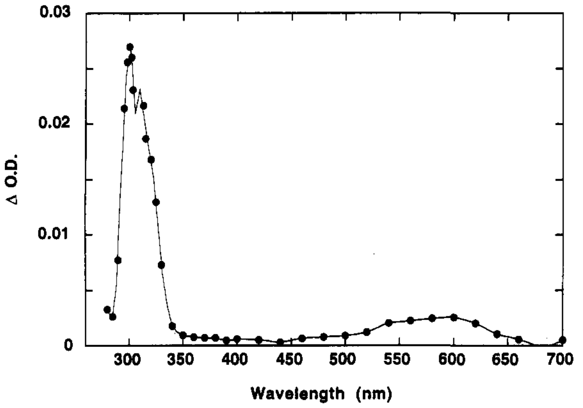

Figure 5. Transient spectrum observed 10 μs after laser flash photolysis (308 nm) of XeF_2 (XeF_4) in hexafluorobenzene under nitrogen.

In order to obtain further evidence for the photochemical generation of $F^•$ from XeF_2, we photolyzed XeF_2 (or XeF_4 in the case of 308 nm excitation, see above) in neat hexafluorobenzene using 308 nm laser excitation. The transient spectrum thus obtained is typical of a cyclohexadienyl radical, with the difference that the long-wavelength absorption band, which is barely detectable in the case of the parent cyclohexadienyl,[13] is easily observed in the case of the heptafluorocyclohexadienyl radical monitored here (Figure 5). Absorption maxima are found at λ_{max} = 300 nm (sharp) and λ_{max} = 600 nm (broad), and the transient decay is predominantly second-order. The first half-life of the transient lifetime is $t_{1/2} \sim 75$ μs under 1 atm of N_2, and it is reduced to 2.2 μs under 1 atm of $^3O_2$, thus yielding a crude rate constant of $k = 1.5 \times 10^7$ M^{-1} s^{-1} for the reaction of $C_6F_7^•$ with $^3O_2$.

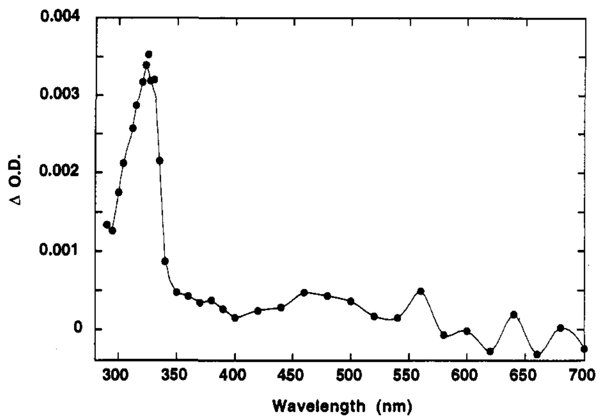

Figure 6. Transient spectrum observed 30 μs after laser flash photolysis (308 nm) of XeF_2 (XeF_4) in Freon-113 containing 10% pentafluoropyridine under nitrogen.

Laser flash photolysis (308 nm) of XeF_2 (XeF_4) in Freon-113 containing 10% pentafluoropyridine gave rise to a transient with λ_{max} = 325 nm, decaying according to second-order kinetics (Figure 6), which we assign to be the hexafluorodihydropyridinyl radical, probably a mixture of the addition products to the 2- and 4-positions. For comparison, the addition product of $HO^•$ to pyridine is reported to have an absorption maximum around 320 nm.[14]

Discussion

Our results show that the primary step in the photocleavage of xenon difluoride in solution is decay into one fluorine atom and a fragment containing xenon, which we assign to be the ground-state xenon monofluoride radical [XeF (X)] on the basis of kinetic and spectroscopic evidence. This assignment deserves some discussion. XeF (X) is known to be a weakly bound molecule with a dissociation energy of only 1065 cm^{-1} (3.05 kcal/mol) in the gas phase.[8] The small blue shift in the absorption spectrum in acetonitrile compared with gas-phase data (~5 nm) may suggest some stabilization of XeF (B) relative to XeF (X) in solution.

Our finding of π complexation with benzene indicates that XeF (X) bears some similarity to the iodine atom, although this analogy should not be overrated. As to the best of our knowledge, XeF (X) had never been detected in solution before; our present results may give a clue on how to further characterize this elusive species.

The rate constants which we could obtain for the reactions of $F^•$, complexed with Freon-113, with a range of substrates clearly demonstrate the extreme reactivity and lack of selectivity of atomic fluorine, as it was already shown for reactions of $F^•$ in the gas phase. Non-diffusion-controlled reactions involving fluorine atoms are about 100 times faster than the corresponding reactions of $Cl^•$, as shown in the case of the reaction with chloroform, where $k_F = 1.8 \times 10^9$ M^{-1} s^{-1}, while $k_{Cl} = 1.8 \times 10^7$ M^{-1} s^{-1}.[2] Diffusion-controlled reactions of $F^•$ proceed with rate constants close to 10^{11} M^{-1} s^{-1}, significantly faster than the reactions of $Cl^•$. We are able to explain these unusually fast reactions in terms of the high diffusion coefficients of second-row atoms, for which the neon atom can be used as a model. The high rate constants also make it obvious that it is not the $(F \leftarrow CF_2Cl\text{–}CFCl_2)$ complex which diffuses and reacts, but rather the reactions are dominated by the "naked" fluorine atom. Presumably $(F \leftarrow CF_2Cl\text{–}CFCl_2)$ is only a rather loose charge transfer (CT) complex, comparable to $(Cl \leftarrow CCl_4)$[2] or $(Br \leftarrow CH_2Br_2)$.[10] The similarity to $(Cl \leftarrow CCl_4)$ is also revealed in the UV absorption spectrum; $(Cl \leftarrow CCl_4)$ is

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reported to have an absorption maximum at 330 nm.[2] Here the similarity between F and Cl complexes is to be anticipated; a similar trend was observed in the series of halogen atom complexes characterized by Treinin and Hayon.[15] The observation that $(F \leftarrow CFCl_3)$ absorbs at higher energies than $(F \leftarrow CCl_2F{-}CF_2Cl)$ comes as a surprise since the latter solvent has the higher ionization potential (11.99 eV for Freon-113 compound with 11.77 eV for $CFCl_3$). In the case of chlorine atoms Chateauneuf[16] has shown that donors with the higher ionization potential lead to shorter absorption maxima. We note that in our case the shift is only 10 nm, close to the resolution (±5 nm) of these measurements. Further, it is possible that in the case of fluorine atom the interaction is more localized, thus following the number (2, 3, or 4) of chlorine atoms at one site.

While monitoring fluorine atom reactivity via its CT complex with Freon-113 may be convenient, a drawback of this "probe" method is the lack of information gained on the site and mode of reaction. In the case of certain quenchers (tetrachloroethylene, methane, water) there is definitely no uncertainty about the mechanism (addition, H-abstraction). In the case of chloroform as reactant, the observed low deuterium isotope effect, $k_H/k_D = 1.88$ at room temperature, probably reflects an early transition state, thereby reducing the influence of isotopic substitution. However, we cannot completely rule out the possibility of chlorine abstraction, which is thermodynamically much less favorable than HF formation. Another rate constant which deserves some comment here is $k = 5.6 \times 10^9\ M^{-1}\ s^{-1}$ for the reaction of $F^\bullet$ with molecular oxygen. Atomic fluorine is the only halogen atom known to rapidly react with $^3O_2$; the gas phase rate constant for the reaction $[F + O_2 \rightarrow FO_2]$ was recently determined to be $k = (1.4 \pm 0.3) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$ $(8.4 \times 10^8\ M^{-1}\ s^{-1})$ which is in the same order of magnitude as the reactions of $F^\bullet$ with relatively unreactive HCFCs such as CF_3CCl_2H and ca. 50 times slower than H-abstraction from methane.[17]

If one compares the rate constant for FO_2 formation with the rate constant $k = 4.1 \times 10^9\ M^{-1}\ s^{-1}$ for O_3 formation from $[^3O + {}^3O_2 \rightarrow O_3]$,[6,7] the difference in reactivity between oxygen and fluorine atoms can be very easily explained in terms of spin statistics: a higher probability of bond formation (1/3) is to be expected for a doublet/triplet reaction than for a triplet/triplet reaction (1/9). We were unable to monitor directly a signal for FO_2, probably because the quantum yield for fluorine atom formation from XeF_2 is low. Even after ca. 100 laser shots with $\lambda = 248$ nm, a change in sample absorbance due to XeF_2 was barely detectable; consistently, the transient absorbance of the heptafluorocyclohexadienyl radical was relatively low, in spite of high extinction coefficients generally observed for the UV bands of cyclohexadienyl radicals. In any event, in our experiments fluorine atoms were produced much less efficiently than in the gas phase experiments conducted by Bott et al.,[9] which may in part be due to their use of high-energy pulses from a 193 nm ArF laser.

Experimental Section

The laser system employed in these experiments has been briefly described in previous publications[3] and is similar to that discussed in detail earlier.[18,19] XeF_2 (Aldrich, used as received) was photolyzed in 7 × 7 mm Suprasil cells using either a Lumonics EX-510 excimer laser operated with $Kr/F_2/He$ (248 nm, ~5 ns, ca. 120 mJ/pulse) or Xe/HCl/Ne (308 nm, ~5 ns, ca. 100 mJ/pulse) or the fourth harmonic of a Surelite Nd-YAG laser (266 nm, ~6 ns, ca. 10 mJ/pulse). Concentrations were ca. 0.6 mM (248, 266 nm excitation) or 6 mM (308 nm excitation). We note that the absorbance in the samples for 308 nm excitation was probably mostly due to XeF_4, which is a 1% impurity in commercial XeF_2 (Aldrich, information provided with the compound). Experiments involving fluorine atom studies were not affected by this; obviously XeF_4 also yields atomic fluorine upon photolysis.

Quenching experiments were performed by injecting deaerated dilute solutions (0.1 or 1%) of quenchers in Freon-113 into carefully deaerated solutions of XeF_2 in Freon-113 (sample volume 3 mL) or by purging solutions of XeF_2 in Freon-113 with various mixtures of N_2 and the quencher gas. This approach was made possible by the fact that XeF_2 is only very insignificantly depleted even upon prolonged photolysis. In the case of water and water-d_2 as quenchers, aliquots of a saturated solution in Freon-113 were added. The solubility of water in Freon-113 was determined by NMR spectroscopy (Bruker 500 MHz, average of 4 samples) employing benzene (0.1%) as an internal standard. The solubility was 2.6 ± 0.3 mM at 20 °C. The solubility of water-d_2 was assumed to be identical to that of water.

Carbon tetrachloride (BDH), Freon-113, and fluorotrichloromethane (Aldrich) were purified twice over alumina prior to use. Acetonitrile (BDH Omnisolv), hexafluorobenzene (Aldrich, 99.9%), and pentafluoropyridine (Aldrich, 99+%) were used as received.

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