Kinetics of the CIO + NO₂ + M Reaction

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The ClO + NO₂ + M reaction has been studied with two techniques: Fourier transform infrared spectroscopy of the products, and flash photolysis-ultraviolet absorption to monitor the decay of ClO in excess NO₂. The measured third-order rate constant is 1.5×10^{-31} cm⁶ molecule⁻² s⁻¹ at 298 K with M = N₂, in good agreement with previous literature values, but the rate constant appears to decrease by up to a factor of 3 in the presence of increasing amounts of OCIO. For the infrared studies a stoichiometric mixture of ClO and NO₂ was prepared in a flow system by mixing NO with OCIO; at least as much NO₂ as ClONO₂ was produced under a variety of experimental conditions. These two sets of results are incompatible with the assumption made in previous kinetic studies that ClONO₂ is the only recombination product; other isomers such as OCIONO or ClOONO are likely to be formed three to four times faster. These results imply that potential stratospheric ozone depletion due to chlorofluoromethanes may be even larger than previously thought.

Introduction

The recombination reaction between NO_2 and ClO radicals is thought to play an important role in stratospheric chemistry in connection with the Cl-atom catalyzed destruction of ozone.^{1,2} A possible product of this reaction is $ClONO_2$, chlorine nitrate (reaction 1). The predominant

$$ClO + NO_2 + M \rightarrow ClONO_2 + M$$
 (1)

destruction process for ClONO₂ in the stratosphere is solar photolysis,³ which occurs relatively slowly (the photodissociation rates range from $\sim 7 \times 10^{-5}$ s⁻¹ at 15 km to 9 × 10^{-4} s⁻¹ at 50 km). Thus, significant amounts of ClONO₂ should accumulate in the stratosphere if reaction 1 has a moderately large third-order rate constant (i.e., if $k_1 > 10^{-31}$ cm⁶ molecule⁻³ s⁻¹). Four groups have studied this reaction by monitoring the pseudo-first-order decay of ClO in the presence of excess NO₂: Leu et al.,⁴ Birks et al.,⁵ and Zahniser et al.⁶ used a low-pressure discharge flow system while Cox and Lewis⁷ used a modulated photolysis technique. The results are in very good agreement ($k_1 \simeq 1.6 \times 10^{-31}$ cm⁶ molecule⁻³ s⁻¹), and all four studies assumed ClONO₂ to be the only recombination product. However, Knauth and co-workers⁸ estimate k_1 to be a factor of 3–4 lower from measurements of the reverse reaction rate constant, k_{-1} , coupled with the thermochemistry, i.e., $k_1 = k_{-1}/K_{ec}$.

A possible explanation for the discrepancy is the existence of multiple pathways in recombination reactions, i.e., the formation of several isomers. For the $Cl + NO_2$ reaction, Niki et al.⁹ found that ClONO (chlorine nitrite) is formed at least four times faster than the more stable isomer, $ClNO_2$ (nitryl chloride), which was previously assumed to be the only product. From calculations of the low-pressure limiting rate constant, Chang et al.¹⁰ conclude that indeed for the $Cl + NO_2$ and $ClO + NO_2$ reactions the less stable isomers should be formed preferentially due to more favorable entropy factors.

In this work we present experimental results which point further to the preferential formation of a less stable isomer of $CIONO_2$ in the $CIO + NO_2$ recombination reaction. We have studied this reaction using a flash photolysis–ultraviolet absorption technique by monitoring the decay of CIO in the presence of excess NO_2 and Cl_2O , as well as excess NO_2 and OCIO, and also by monitoring the infrared spectra

[‡]Department of Chemistry, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo, Japan. of the reaction products on a millisecond time scale with a Fourier transform IR-fast flow technique developed in our laboratory.

Experimental Section

Flash Photolysis Apparatus. Figure 1 shows a schematic diagram of the flash photolysis-ultraviolet absorption apparatus. The 2.5-cm diameter, 73-cm long photolysis cell was made out of Suprasil quartz. The Xe-filled flash lamp was operated at a repetition rate of 0.2-1 Hz and the flash duration was $\sim 20 \ \mu s$.

The ClO concentration was monitored by following the time-resolved attenuation of the probe light supplied by a 100-W high-pressure Xe arc lamp, which traversed the photolysis cell 6 times by reflection from external White cell optics before being focussed onto the entrance slit of a 0.45-m monochromator (McKee-Pedersen 1018B), with a typical resolution of 0.18 nm. The signal, detected by an EMI-9782 QA photomultiplier as photon counts, was processed by a signal averager-computer system (Inotech-Ultima II, Data General-Nova 3) operated in the multichannel scaling mode. The kinetic decay curves were accumulated from 20 to 300 flashes to improve the signal-to-noise ratio and were followed typically over three half-lives. A gating circuit was used to reduce saturation of the photomultiplier dynode chain by scattered light from the flash lamp.

For some of the experiments the probe light was generated by a pulsed dye laser (Chromatix CMX-4) and the kinetic decay curves were obtained by varying the time delay between the laser and the flash lamp. The procedure to acquire and manipulate the laser signals has been described elsewhere.¹¹ In comparison with the Xe-lamp data, the laser results were more scattered due to baseline instabilities but were otherwise identical.

In order to avoid the accumulation of photolysis and reaction products we performed all experiments by flowing the reactants through the photolysis cell, the residence time being ~ 1 s. The reactants were mixed just before entering the cell. All experiments were carried out at 298 K.

Infrared Absorption Apparatus. The IR spectra were recorded with a Nicolet 7199A Fourier transform infrared spectrometer equipped with a standard data handling system and a liquid- N_2 cooled HgCdTe detector. A 50-cm long, 2.5-cm diameter Pyrex absorption cell fitted with AgCl windows was used with four passes. The spectra were taken at 1-cm⁻¹ resolution, each one being computed from

Dreyfus Teacher–Scholar.



Figure 1. Schematic diagram of the flash photolysis-UV absorption apparatus.



Figure 2. Typical first-order plots for [CiO] in the presence of various excess concentrations of NO₂: $[N_2] = 20$ torr; $[Cl_2O] = 0.13$ torr.

the average of 64 interferograms. The concentrations of the various components were obtained by subtraction of reference spectra.

The reactants were introduced into the IR absorption cell as described above for the flash photolysis experiments; the residence time in the cell ranged from 30 to 500 ms.

Chemicals. N_2 , Cl_2 , NO_2 , and NO (Matheson Gas Products) were used without further purification. All gases were handled on a greaseless glass-Teflon vacuum line equipped with MKS capacitance manometers.

Since the experiment required significant amounts of Cl_2O and of OClO—which is explosive—these chemicals were generated continuously by flowing a Cl_2/N_2 mixture through a column packed with solid NaClO₂ (to produce OClO) or with yellow mercuric oxide (to produce Cl_2O). The efficiency of the conversion and the purity and concentration of all reactants was continuously monitored by UV absorption spectroscopy by means of a Cary 219 spectrophotometer fitted with a long-path cell connected in series with the main gas flow. The flow system could be operated under stable conditions for periods of several hours.

Results

Flash Photolysis Experiments. The kinetic studies were carried out under pseudo-first-order conditions ($[NO_2] >$ 10[ClO]), so that a knowledge of the absolute concentration of ClO was not required. Figure 2 shows some typical logarithmic plots of the absorption signal vs. time, and Figure 3 shows the variation of the pseudo-first-order rate constant with [NO₂]. The ClO concentration was followed for at least one order of magnitude decrease, and the rate constant values were computed by means of linear leastsquares fits to the signals, starting 0.5–1 ms after the photolytic flash. The results are summarized in Tables



Figure 3. Pseudo-first-order rate constant k^1 vs. [NO₂]; [Cl₂O] = 0.03-0.43 torr.

 TABLE I:
 Summary of Flash Photolysis-UV

 Absorption Experimental Conditions and Results,
 Using Cl.O as a ClO Source

no. of experi- ments	total press., torr	$[Cl_2O]$ range, torr	[NO ₂] range, torr	$\frac{10^{32}k_4,^a}{\text{cm}^6 \text{ mole-} \\ \text{cule}^{-2} \text{ s}^{-1}}$
10 32 6	20 20 20	<0.08 0.08-0.13 0.13-0.43	0.07-0.26 0.05-0.27 0.07-0.19 av:	$\begin{array}{c} 15.1 \pm 1.2 \\ 15.1 \pm 1.3 \\ 14.5 \pm 0.9 \\ 15.0 \pm 1.2 \end{array}$
3 12	100 100	0.05 0.11-0.12	0.06-0.11 0.03-0.10 av:	11.2 ± 1.0 11.4 ± 0.7 11.3 ± 0.7

^a The error bars represent one standard deviation.

TABLE II: Summary of Flash Photolysis-UV Absorption Experimental Conditions and Results, Using OCIO as a CIO Source

no. of experi- ments	total press., torr	[OClO], torr	[NO ₂] range, torr	$\frac{10^{32}k_{4}^{\ a}}{\text{cm}^{6} \text{ mole-} \\ \text{cule}^{-2} \text{ s}^{-1}}$
23	20	0.47	0.22-0.43	8.1 ± 0.7
20	20	0.36	0.12-0.38	8.7 ± 0.9
21	20	0.21	0.12 - 0.37	10.5 ± 0.6
17	20	0.10	0.09-0.37	12.9 ± 1.2
14	20	0.06	0.08-0.29	13.5 ± 0.6
20	100	0.45	0.02-0.31	5.7 ± 0.5
11	100	0.30	0.05-0.18	6.8 ± 0.3
17	100	0.23	0.04-0.24	7.9 ± 0.8
15	100	0.11	0.04-0.14	8.5 ± 0.9

^a The error bars represent one standard deviation.

I and II for experiments employing Cl₂O and OClO, respectively, as photolytic ClO sources. In these experiments the ClO concentration was monitored by absorption of the probe light at 277.2 nm, corresponding to the (11,0) band head of the $A^2\pi$ -x² π system. The initial ClO concentration was estimated by assuming an absorption cross section of 7.2 × 10⁻¹⁸ cm² at this wavelength.¹²

Preliminary control experiments were carried out by recording signals at various flow rates, flash repetition rates, flash energies, reactant concentrations, etc.; in all cases the signal behavior did correspond to a pseudofirst-order ClO decay (except on a time scale shorter than 1 ms, as discussed below). Furthermore, the signal was monitored at wavelengths corresponding to different ClO band heads, or to a minimum between band heads, be-

TABLE III:Summary of Experimental Conditions andResults for the Fourier Transform IR-Fast Flow Study

total press., torr	residence time, ms	$10^{3} \cdot \\ [OClO]_{\circ}, \\ torr$	10 ³ . [NO] ₀ , torr	[CIONO ₂]/ [NO ₂]
20	340	17	16	0.8
20	340	19	6	0.8
20	140	77	23	0.5
20	140	77	55	1.0
20	140	77	10	1.2
20	140	77	76	0.4
100	100	62	26	1.1
100	140	68	76	0.3
100	500	272	122	0.3
100	100	59	23	0.7

tween 272 and 300 nm; the same rate constant values were obtained in these experiments, and the ClO concentrations calculated from the known ClO absorption cross sections at the various wavelengths¹² agreed within experimental error.

The amount of NO₂ photolyzed by the flash was determined from a measurement of the absorption of the probe light at 488.6 nm; it was less than 5% in all cases. No change in the ClO concentration could be observed in the absence of NO₂ on the time scale of our measurements (\sim 30 ms).

Fourier-Transform Infrared Experiments. Samples of NO in N₂ and OCIO in N₂ were mixed just before flowing into the IR-absorption cell. The reaction conditions and the observed [ClONO₂]/[NO₂] product ratios are summarized in Table III for the experiments with residence times of 100 ms or longer. In these experiments the spectra showed no evidence for the formation of products other than NO₂, ClONO₂, and small amounts of ClONO. Within experimental error, these three species accounted for all the NO added; in contrast, ClONO₂ and ClONO did not account for the amount of OCIO that disappeared; presumably Cl₂ and O₂ were also formed. A few experiments with a residence time of ~30 ms were also carried out; some as yet unidentified bands began to appear indicating the presence of additional IR-absorbing species.

Discussion

Flash Photolysis with Cl_2O as a ClO Source. The main chemical reactions expected to occur in this system are the following:

$$Cl_2O + h\nu \rightarrow Cl + ClO$$
 (2)

$$Cl + Cl_2O \rightarrow Cl_2 + ClO$$
 (3)

$$ClO + NO_2 + M \rightarrow products$$
 (4)

The NO₂ concentration was adjusted so that the ClO decay occurred on a 3–10-ms time scale; since reaction 3 is extremely fast,¹³ after the initial 50 μ s only reaction 4 should contribute to this decay. The reaction of ClO with itself is too slow to be of importance under our experimental conditions (the initial ClO concentration ranged from 0.8 to 6 mtorr, corresponding to decay times longer than 100 ms for the ClO + ClO reaction).¹⁴

Photolysis of NO_2 occurred to a minor extent in our experiments so that the following reactions, for which the rate constants are well-known,² should be considered:

$$NO_2 + h\nu \rightarrow NO + O$$
 (5)

$$O + NO_2 \rightarrow O_2 + NO \tag{6}$$

$$NO + ClO \rightarrow NO_2 + Cl$$
 (7)

Reactions 5 and 6 occur predominantly in the first 50 μ s, and reaction 7 has no net kinetic effect on ClO, since



Figure 4. Apparent third-order rate constant k_4 as a function of the concentration of Cl₂O and of OCIO.

the Cl atoms produced react very rapidly with Cl_2O (reaction 3), regenerating the ClO radicals. Thus, no complications should arise from photodissociation of NO_2 in our system.

As shown in Table I, the third-order rate constant obtained from our data at 20 torr is $k_4 = 1.5 \times 10^{-31}$ cm⁶ molecule⁻² s⁻¹, in good agreement with the average of the low-pressure values reported in the literature, i.e., $k_1 = 1.6 \times 10^{-31}$ cm⁶ molecule⁻² s⁻¹ at 298 K. Our k_4 value at 100 torr is ~20% smaller than the 20-torr value, whereas the Cox and Lewis' study—the only other one carried out at pressures above 10 torr—indicates a drop of only ~8%.⁷ Perhaps the discrepancy can be attributed to experimental scatter; Cox and Lewis had to apply a somewhat uncertain correction factor to account for appreciable concentration gradients along their photolysis cell.

There are two theoretical calculations predicting significant falloff in k_1 , starting at ~20 torr,¹⁵ a result which appears to be in agreement with our experimental observations. However, for a meaningful comparison the identity of the products has to be first established, and this identity is in question, as discussed below.

Flash Photolysis with OClO as a ClO Source. Here again, a set of fast reactions with reasonably well-established rate constants² occur initially, so that ~ 1 ms after the photolytic flash the system should only contain negligible amounts of species other than ClO, NO₂, OClO, and N₂. These reactions include reactions 5–7 and the following:

$$OClO + h\nu \to O + ClO \tag{8}$$

$$NO + OCIO \rightarrow NO_2 + CIO$$
 (9)

$$Cl + OClO \rightarrow ClO + ClO$$
 (10)

The rate-limiting step for this initial phase is reaction 9, and the net effect of reactions 7 and 10 is to accelerate reaction 9. The initial increase in ClO concentration due to reactions 9 and 10 was confirmed experimentally in our system.

Figure 4 illustrates the behavior of the apparent thirdorder rate constant k_4 as a function of OCIO concentration; for comparison the Cl₂O results are also shown in the figure. Within experimental error the same result is obtained with both ClO sources, if the OCIO pressure is small enough; however, as the OCIO concentration is increased, k_4 decreases by up to a factor of 2-3.¹⁶

TABLE IV:Rate Constants Employed in the ComputerSimulation of the NO + OCIO Reaction at 298 K

reaction	k ^{a, b}
$NO + OClO \rightarrow NO_2 + ClO$	3.4×10^{-13}
$NO + ClO \rightarrow NO_2 + Cl$	1.8×10^{-11}
$Cl + OClO \rightarrow ClO + ClO$	6.0×10^{-11}
$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$	2.2×10^{-13}
$ClO + ClO \rightarrow Cl + OClO$	$2.0 imes 10^{-14}$
$Cl + NO_2 + N_2 \rightarrow ClONO + N_2$	$1.5 imes 10^{-30}$
$ClO + NO_2 + N_2 \rightarrow ClONO_2 + N_2$	1.5×10^{-31}

^a Units: cm^3 molecule⁻¹ s⁻¹, except last two: cm^6 molecule⁻² s⁻¹. ^b From ref 2.

One possible explanation of this result is that the excess OCIO interacts in some way with CIO reducing its apparent reactivity toward NO₂. Yet, as stated earlier, experiments carried out in the absence of NO₂ showed that the CIO concentration remained constant on the time scale of the measurement even if OCIO was present in large excess. This observation does not rule out the very rapid formation of small equilibrium amounts of Cl_2O_3 , which is a rather unstable species:¹⁷

$$ClO + OClO + M \rightleftharpoons Cl_2O_3 + M$$
 (11)

However, the presence of Cl_2O_3 cannot explain a decrease in k_4 , since only a small and nearly constant fraction of the ClO would be tied up as Cl_2O_3 (in contrast, an increase in k_4 could be easily explained, e.g., by assuming a fast bimolecular reaction between Cl_2O_3 and NO_2).

Yet another explanation is that the initial amount of NO₂ is reduced in proportion to the amount of OClO present. However, the thermal reaction between NO₂ and OClO is too slow to be of importance under our experimental conditions.¹⁸ Furthermore, the experiments show that the decrease in k_4 is independent of flash energy so that this effect is not likely to be due to secondary photolysis reactions. Similarly, the reactions of ClONO₂ with OClO, Cl₂O, NO₂, or NO are too slow to have any consequence in our system.

A more plausible explanation for the decrease in k_4 appears to be that a recombination product other than ClONO₂ reacts with OClO, in one or more steps, regenerating a ClO radical:

$$ClO + NO_2 + M \rightarrow ClONO_2 + M$$
 (1)

$$ClO + NO_2 + M \rightarrow (ClNO_3) + M$$
 (12)

$$OClO + (ClNO_3) \rightarrow ClO + products$$
 (13)

where (ClNO₃) represents a hypothetical chlorine nitrate isomer. The dashed line in Figure 4 is the result of a simulation of this mechanism, assuming $k_1 = 6 \times 10^{-32}$ cm⁶ molecule⁻² s⁻¹, $k_{12} = 9 \times 10^{-32}$ cm⁶ molecule⁻² s⁻¹, and k_{13} $= 2 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹. This latter rate constant is unusually large for a reaction between OClO and a nonradical species. The chemistry of the unstable isomer might indeed be unusual, although a preexponential factor $>10^{-14}$ cm³ molecule⁻¹ s⁻¹ is plausible if reaction 13 is a metathesis.

Infrared Product Analysis. The reaction between NO and OClO (reaction 9) produces initially a 1:1 mixture of NO₂ and ClO radicals. This mixture should yield a stoichiometric amount of ClONO₂ if reaction 1 is the only important channel for recombination and if no other secondary reactions take place. In order to examine this latter assumption we computer simulated the kinetics in these experiments using the CHEMK program¹⁹ and the reaction scheme presented in Table IV. The [ClONO₂]/[NO₂] product ratio is calculated to be greater than ten for a reactant ratio [OClO]/[NO] \geq 3, and greater

than six if $[OCIO]/[NO] \ge 1$; yet, as may be seen in Table III, in most experiments the amount of ClONO₂ produced was smaller than the amount of NO₂ produced. As mentioned earlier, reactions such as $ClO + ClO \rightarrow Cl_2 + O_2$, $ClONO_2 + NO \rightarrow products, ClONO_2 + OClO \rightarrow products,$ or NO + Cl (+M) \rightarrow NOCl (+M) are unimportant under our experimental conditions, and only Cl atoms are capable of destroying ClONO₂ molecules under these conditions. However, Cl atoms react much more rapidly with OClO so that only a small fraction of the ClONO₂ formed can be consumed by this route. Clearly, the assumption that $ClONO_2$ is the only recombination product (reaction 1) is incompatible with our observations, and a much more reactive species must be formed predominantly, a species which on the time scale of our experiments yields Cl_2 , O_2 , NO₂, and perhaps also ClONO₂.

Chlorine Nitrate Isomers. Our UV and IR results indicate that reaction 4 produces a species other than ClO- NO_2 at least twice as fast as it produces $ClONO_2$, but we have not obtained so far sufficient information to establish the identity of this unknown product. In fact, the flash photolysis UV-absorption experiment shows that this species reacts very rapidly with OClO and hence it should not be present in measurable quantities in our IR absorption cell. (We are planning to carry out some additional higher sensitivity IR experiments to monitor the ClO + NO_2 reaction products in the absence of OClO.)

The following are, in principle, possible channels in the $CIO + NO_2$ reaction:

$$ClO + NO_2 + M \rightarrow ClONO_2 + M$$
 (1)

$$\rightarrow \text{OClNO}_2 + M$$
 (14)

$$\rightarrow$$
 ClOONO + M (15)

 \rightarrow OClONO + M (16)

$$ClO + NO_2 \rightarrow Cl + NO_3$$
 (17)

$$\rightarrow$$
 ClOO + NO (18)

$$\rightarrow$$
 OClO + NO (19)

$$\rightarrow \text{ClNO}_2 + 0$$
 (20)

$$\rightarrow$$
 ClNO + O₂ (21)

Reactions 17-21 are bimolecular, whereas at low pressures the reaction is observed to be third order. Furthermore, reactions 17-20 are endothermic by about 14, 10, 14, and 30 kcal/mol, respectively. Reaction 21 is \sim 20 kcal/mol exothermic but is not likely to be a fast reaction since two bonds have to be broken and two new bonds have to be formed simultaneously.

Knauth and co-workers⁸ suggested OCINO₂ as a possible product (reaction 14) and explained the apparent formation of ClONO₂ as the only product in their experiments by assuming that OCINO₂ reacted with excess NO₂ to produce ClONO₂ on a time scale of minutes. Chang et al.¹⁰ suggested ClOONO as a likely product (reaction 15) on the basis of calculated low-pressure rate constants. We suggest here a third possibility, namely, OCIONO (reaction 16); such an isomer would also be expected to form faster than ClONO₂ (and OCINO₂) on the basis of arguments analogous to those put forward by Chang et al.,¹⁰ and it would also be capable of reacting with NO₂ to produce ClONO₂, thus explaining Knauth's results. If we assume that indeed OCIONO is formed, reaction 13 could be written as follows:

$$OClO + OClONO \rightarrow OCl + O_2ClONO$$
 (22)

The compounds O_3 ClONO (nitrosyl perchlorate) and O_3 ClONO₂ (nitryl perchlorate) are stable and are reason-

ably well characterized;²⁰ ClONO is also well characterized²¹ and is not as stable. One can consider ClONO, OCIONO, O₂CIONO, and O₃CIONO to be compounds derived from hypochlorous, chlorous, chloric, and perchloric acids, respectively. Chlorous and chloric acids have been identified only in solution;²² the gaseous compounds should be thermodynamically stable, but they are likely to disproportionate very rapidly. From this point of view reaction 22 appears plausible and our infrared results could be explained by assuming that these compounds are destroyed under our experimental conditions, ultimately yielding Cl_2 , NO_2 , and O_2 . On the other hand, reaction 22 is clearly rather speculative since neither OCIONO nor O₂ClONO have been characterized yet. These two compounds might be thermodynamically quite stable and yet difficult to identify due to their presumably high chemical reactivity.

Atmospheric Implications. Chlorine nitrate functions as a relatively efficient holding tank for stratospheric chlorine due to its slow solar photodissociation rate. In contrast, OCIONO and CIOONO are nitrites so that they can be expected to decompose considerably faster in the atmosphere; one of the characteristic absorption bands of nitrites lies in the 300-450-nm range.²³ In fact, the formation of species containing Cl, N, and O atoms-e.g., CINO, CINO₂, CIONO, but not CIONO₂-need not even be considered in most stratospheric calculations due to their fast photodissociation rates. Hence, it is reasonable to assume that the chlorine nitrate isomer formed in reaction 4 will play at most a minor role as an inert chlorine reservoir in the stratosphere, although this isomer might be involved in a catalytic cycle of some importance if its photolysis products are species other than ClO and NO₂.

In summary, our results indicate that the formation rate of ClONO₂ in the stratosphere has been overestimated in the past by a factor of 3 or more, so that potential stratospheric ozone depletion due to chlorofluoromethanes may be even larger than previously thought. The rate of the reaction between ClO and NO_2 at low pressures appears to be reasonably well established, but more work remains to be done to elucidate the properties and the identity of the products.

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