# The Reaction of Chlorine Monoxide with Cyclohexene. A Molecule Induced Homolysis Reaction<sup>1</sup>

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DENNIS D. TANNER, NESTOR NYCHKA, and TAMEICHI OCHIAI. Can. J. Chem. 52, 2573 (1974). The reaction of chlorine monoxide with cyclohexene at  $-20^{\circ}$  in the dark was found to proceed by an addition reaction to yield *trans*-2-chlorocyclohexyl hypochlorite. Concomitant with the addition, a molecule induced homolysis reaction of the chlorine monoxide occurs with cyclohexene to produce a number of free radical substitution and addition products, as well as products possibly arising from ionic addition reactions. Induced halogenation was found with added cyclohexane.

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On a trouvé que la réaction du monoxyde de chlore avec le cyclohexène à  $-20^{\circ}$  dans l'obscurité conduit par une réaction d'addition à l'hypochlorite du chloro-2 cyclohexyl-*trans*. Simultanément à l'addition une réaction homolytique induite par la molécule permet au monoxyde de chlore de réagir avec le cyclohexène pour fournir un certain nombre de produits de substitution radicalaires et d'additions de même que des produits provenant possiblement de réactions d'addition ioniques. En présence de cyclohexane on a trouvé des réactions d'halogénation induites. [Traduit par le journal]

### Introduction

The photoinitiated reaction of carbon tetrachloride solutions of chlorine monoxide with saturated alkanes has been shown to be a free radical chain halogenation having the overall stoichiometry:  $2RH + Cl_2O \rightarrow 2RCl + H_2O$ . The mechanism of the reaction has been proposed to proceed through a mixed chain (Scheme 1) involving OCl, (*a*), and chlorine and/or hydroxy radicals, (*b*), as the chain-propagating species (1).

(a)

(b)

$$\begin{aligned} \text{HCl} + \text{HOCl} \rightleftarrows \text{HOH} + \text{Cl}_2 \\ \text{R} \cdot + \text{Cl}_2 \to \text{RCl} + \text{Cl} \cdot \end{aligned}$$

 $RH + \cdot OCl \rightarrow R \cdot + HOCl$ 

 $R \cdot + Cl_2O \rightarrow RCl + \cdot OCl$ 

 $2HOCl \rightleftharpoons H_2O + Cl_2O$ 

 $RH + Cl \cdot \rightarrow R \cdot + HCl$ 

and/or

$$R^{+} + HOCl \rightarrow RCl + \cdot OH$$

### Scheme 1

The reaction was found to be thermally initiated slowly in the dark at  $40^{\circ}$ .

 $Cl_2O \rightarrow Cl \cdot + \cdot OCl$ 

The overall reactivity of the reagent, with saturated alkanes, was found to be similar to that of t-butyl hypochlorite (1) and an obvious extension of the investigation of its reactions with organic materials was an investigation of its reactivity with unsaturated hydrocarbons.

#### Results

The addition of a carbon tetrachloride solution of chlorine monoxide to a large excess of cyclohexene at 40 to  $-20^{\circ}$  resulted in an instantaneous reaction; no color due to chlorine monoxide ever developed in the solutions. The reaction was spontaneous and exothermic at  $-20^{\circ}$  in the absence of light. Addition of atmospheric oxygen did not appear to qualitatively inhibit the rate of the reaction. The titer for active halogen dropped on initial mixing to 31% and after 20 h was still 27% of the titer of the starting chlorine monoxide. Analysis and isolation of the resultant products from the reaction mixtures after titration showed, in addition to water, both addition and substitution products, accounting for all of the chlorine initially added as chlorine monoxide, (see Table 1). Karl-Fischer titration of reactions carried out at ambient temperature showed  $0.50 \pm 0.03$  mol of water were produced for every mole of chlorine monoxide. The minor products (5-9) were present in amounts large enough to detect and identify by a comparison

<sup>&</sup>lt;sup>1</sup>Taken in part from the M.Sc. thesis of Nestor Nychka, University of Alberta, 1969.

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TABLE 1. Products of the dark reaction of cyclohexene with chlorine monoxide in carbon tetrachloride<sup>a</sup>

	Yield	
Products	$(\text{mol/mol of } \text{Cl}_2\text{O}^{\flat})$	
3-Chlorocyclohexene (1)	$0.79 \pm 0.01$	
trans-2-Chlorocyclohexanol (2)	$0.53 \pm 0.02$	
<i>trans</i> -1,2-Dichlorocyclohexane (3)	$0.082 \pm 0.008$	
2,2'-Dichlorocyclohexyl ether (4)	0.115	
4-Chlorocyclohexene (5)	$0.026 \pm 0.012$	
2-Chlorocyclohexanone (6)	$0.027 \pm 0.009$	
1-Chlorocyclohexene (7)	0.01	
2-Cyclohexenone (8)	$0.027 \pm 0.007$	
2-Cyclohexenol (9)	$0.040 \pm 0.009$	
Unidentified products	0.056	
Remaining active halogen <sup>c</sup>	0.272	

<sup>a</sup>The reactions of 0.3 *M* chlorine monoxide with cyclohexene (1:10 mol ratio) were carried out at  $-20^{\circ}$ . <sup>b</sup>Errors reported are deviations from the average values obtained from three or more independent experimental determinations. The product yields are those determined after titration for active halogen. Since no color for Cl<sub>2</sub>O was detectable, the active halogen was presumably in the form of the alkyl hypochlorite (ROCl), 10.

of their g.l.p.c. retention times (two columns) with those of authentic materials but were present in amounts too small to isolate. One of the minor products, 4-chlorocyclohexene, was not only identified by its g.l.p.c. retention time (three columns) but its mass spectrum was shown to be identical to that of an authentic sample. Compound 6, 2-chlorocyclohexanone, was found (g.l.p.c.) to react with 2,4-dinitrophenylhydrazine when the reaction mixture was shaken with that reagent. Small amounts of other products, designated as unidentified products in Table 1, were shown by g.l.p.c. to be present in the reaction mixture. Some of these unidentified products decomposed slowly at room temperature to give increasing amounts of products 8 and 9. No cis-1,2-dichlorocyclohexane, cis-2chlorocyclohexanol, cyclohexanol, or cyclohexene oxide were detected as products.

Since the dichlorocyclohexyl ether has four centers of substitution, seven stereoisomers are possible. No stereochemical characterization of the ether products was attempted; it was noted, however, that analysis by g.l.p.c. showed the ether products to be composed of at least three isomers.

Aqueous solutions of hypochlorous acid were used to synthesize authentic samples of trans-2chlorocyclohexanol, 2. When aqueous hypochlorous acid was allowed to react with carbon tetrachloride solutions of cyclohexene  $(-20^{\circ})$ , dark), not only was the expected major product, 2, found but lesser amounts of 1, 3, 4, and 5 were also produced.

When cyclohexane was added to the cyclohexene before its reaction with chlorine monoxide, induced halogenation of the saturated material accompanied the reaction of the unsaturated olefin. The yield of cyclohexyl chloride formed in these induced halogenations was diminished by the addition of molecular oxygen (see Table 2).

When the ratio of initially added cyclohexene to chlorine monoxide was varied from 3.5:1 to 35:1 the yield of three of the major products (2–4) remained relatively constant while the yield of 3-chlorocyclohexene, 1, increased with increased olefin concentration. The yield of 1

TABLE 2. The production of chlorocyclohexane during the reaction of chlorine monoxide with cyclohexane in the presence of cyclohexene<sup>a</sup>

Concentration (relative amounts)		Yield (mol yield $C_6H_{11}Cl/mol Cl_2O$ )		
$C_{6}H_{12}$	$C_{6}H_{10}$	Cl <sub>2</sub> O	Degassed	Not degassed
9.3	2	1.0	$0.05 \pm 0.005$ (0.06) <sup>b</sup>	
9.2	1	1.0	$0.059 \pm 0.004$ (0.14 $\pm 0.02$ ) <sup>b</sup>	
9.1	0.4	1.0	$0.14 \pm 0.02$	
9.2	0.4	1.0	0.13	0.08
9.3	0.2	1.0	0.10	
9.1	0.017	1.0	$0.21 \pm 0.06$	$0.076 \pm 0.016$
10		1.0	$0.063 \pm 0.018$	$0.006 \pm 0.001$

<sup>a</sup>All reactions were quenched immediately after mixing at  $-20^{\circ}$ . Experimental deviations are from two independent experiments. <sup>b</sup>Values in parenthesis were obtained after 20-h reaction at  $-20^{\circ}$ .

obtained under these conditions was decreased by the addition of molecular oxygen, (see Table 3).

### Discussion

The apparently spontaneous reaction of chlorine monoxide with cyclohexene was similar to other chlorination reactions with reagents capable of undergoing both free radical and ionic addition reactions with unsaturated hydrocarbons (2,3). The major product 3-chlorocyclohexene, 1, has long been recognized as being the product of both ionic addition and free radical substitution (4). The formation of 4-chlorocyclohexene, 5, however, was indicative of a free radical substitution process, since no ionic pathway to its formation is available (2). Further substantiation of the radical nature of the major portion of the reaction was obtained by observing the effect of molecular oxygen on the relative rates of formation of the four major products (1-4), see Table 3. The yield of the major product 3-chlorocyclohexene was markedly reduced by the presence of oxygen and it could be inferred that its formation, at least in part, was the result of a free radical chain chlorination which was inhibited by oxygen. A free radical chain chlorination process for the reaction of chlorine monoxide with cyclohexene  $(-20^{\circ})$  was firmly established by observing the facile induced chlorination of added cyclohexane, a reaction which itself only proceeds slowly by a free radical path with this reagent, see Table 2.

The observation that the rate of free radical substitution of cyclohexane (see Table 2) was

dependent upon the concentration of added cyclohexene was indicative of a molecule induced initiation reaction. Molecule induced homolyses have been shown to occur in the liquid phase dark chlorination of olefins with molecular chlorine (2). In the molecular chlorine chlorination of cyclohexene it was demonstrated that the products 1, 3, 7, and 5 were formed by competitive ionic and free radical paths whose relative importance could be modified by molecular oxygen. The addition of cyclohexane, as in the case of chlorine monoxide, led to induced halogenation. The free radical chain chlorination was found to be dependent upon the concentration of the cyclohexene. The dependence of the radical path on the concentration of the olefin was interpreted as being due to an initiation step which had a greater than first order dependence



on cyclohexene. A similar type of initiation process has been proposed to explain the spontaneous dark halogenation reactions of *t*-butyl hypochlorite and hypobromite with styrene and 2-butyne (3).

Thermodynamic arguments have been presented to justify the proposal that the formation of radicals directly from the reactants would overcome the activation energy necessary for the homolysis of the halogenation reagent (2,3). By analogy, a dissociation energy, D(Cl-OCl), equal to 21.7–25.1 kcal/mol (5) could be overcome by the interaction of chlorine monoxide with cyclohexene to form radicals in an exo-

$$\bigcirc + \operatorname{Cl}_2 O \rightarrow \bigcirc \cdot^{\operatorname{Cl}} + \cdot \operatorname{OCl}$$

thermic process.<sup>3</sup> A reaction which is bimolecular in olefin would be even more highly exothermic.<sup>4</sup>



<sup>3</sup>The enthalpy for addition of a chlorine atom to cyclohexene has been estimated by Poutsma (2) to be -26kcal/mol. The enthalpy for the initiation reaction can be calculated for the reaction of chlorine monoxide and cyclohexene to be exothermic  $\Delta H = (D(\text{CIO}-\text{CI})-26) =$ -1 to -4 kcal/mol.

<sup>4</sup>The enthalpy for the reaction for the addition of OClto cyclohexene can be estimated at >26 kcal/mol since generally D(R-Cl) < D(R-OH). The trimolecular process would be exothermic by >27 to 31 kcal/mol since two radicals are formed in the process.

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Mol excess of cyclohexene <sup>a</sup>	Products (mol/mol Cl <sub>2</sub> O) <sup>b</sup>				
	1	2	3	4	
3.5, degassed	0.59	0.50	0.11	0.194	
10, degassed	$0.79 \pm 0.01$	$0.53 \pm 0.02$	$0.082 \pm 0.008$	0.115	
10, not degassed	$0.38 \pm 0.03$	$0.53 \pm 0.02$	$0.105 \pm 0.01$	0.124	
35, degassed	$0.95 \pm 0.05$	$0.50 \pm 0.03$	$0.063 \pm 0.006$	0.092	
35, not degassed	$0.66 \pm 0.09$	$0.50 \pm 0.03$	$0.078 \pm 0.026$	0.105	

TABLE 3. Distribution of major products (>4%) from the reaction between cyclohexene and chlorine monoxide at various olefin concentrations ( $-20^{\circ}$ , dark, CCl<sub>4</sub> solvent)

<sup>a</sup>Mol excess with respect to Cl<sub>2</sub>O. Reactions were carried out in degassed ampoules or ampoules containing atmospheric amounts of oxygen (not degassed). <sup>b</sup>Errors are deviations from the mean of at least three independent experiments.

It can be seen in Table 3 that as the olefin concentration increased the production of 1 was also steadily increased, suggesting that the radical production of 1 involved an initiation step that is higher than first order in olefin.

The observation that the initial titer for active halogen fall to 31% upon mixing and remains relatively constant for 20 h, militates for the formation of a positive halogen species which can coexist under the reaction condition with large amounts of cyclohexene. Since the color of chlorine monoxide immediately fades on mixing and since both molecular chlorine and hypochlorous acid react rapidly with cyclohexene under the reaction conditions; the secondary hypochlorite from the addition of chlorine monoxide to the olefin appears to be a candidate for the active halogen containing compound.



Some evidence that the secondary hypochlorite, 10, is a product of the reaction can be obtained by an examination of the reaction products after titration. The formation of *trans*-2-chlorocyclohexanol, 2, as a major product found after titration can be rationalized as arising at least in part from the reductive hydrolysis of 10. The formation of 2 has also been shown to arise from the addition of hypochlorous acid (formed as the product from the homolytic reactions of chlorine monoxide) to cyclohexene and would also be formed from the homolytic halogenation reactions of 10 as well. The amount of 2 arising from 10 after hydrolysis must be at least equal to the titer for active halogen. The ether, 4, derived from the addition of 10 to cyclohexene, is proposed to arise from the free radical reaction of the reactants since after mixing the titer for active halogen remains even in the presence of a large excess of cyclohexene and therefore precludes a rapid ionic pathway.



Ether formation from hypochlorite addition to olefins has precedent in the free radical reactions of *t*-butyl hypochlorite, where as high as 17% addition accompanies allylic substitution (6). Chloroethers and 1,2-dichlorides, analogous to 1,2-dichlorocyclohexane, **3**, are also formed in the molecule induced homolytic reaction of *t*-butyl hypochlorite with styrene and disubstituted acetylenes (3).

The formation of 2-chlorocyclohexanone, 6, is likewise easily rationalized on the basis of intermediate 10, since carbonyl compounds are the major products from the radical decomposition of primary and secondary alkyl hypochlorites (7–9).

A schematic summary of the reactive pathways described which accounts for >96% of the reaction products is given in Scheme 2.

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### Experimental

### Materials

Phillips 66 research grade (99.94 mol%) cyclohexene was used without purification; its purity was checked by g.l.p.c. "Freon 112" (tetrachlorodifluoroethane) was distilled through an 18 in. column containing glass helices and the middle fraction collected. Carbon tetrachloride was distilled from phosphorus pentoxide. Cyclohexane was spectroquality reagent grade (Matheson, Coleman, and Bell) and its purity checked by g.l.p.c. before use. Chlorine monoxide was prepared and analyzed as described previously (1). Concentrations of chlorine monoxide from 0.15 to 0.5 M were used in the reactions. Aqueous solutions of hypochlorous acid, free of chlorine monoxide and molecular chlorine, were prepared as previously reported (1). All glassware was chromic acid washed, rinsed with ammonia, then water, and dried before use.

### **Reaction Procedure**

In most reactions, 2 ml of a carbon tetrachloride solution of chlorine monoxide (0.3 M) were degassed, in the absence of light, in a Pyrex breakseal containing a degassed sample of cyclohexene above the breakseal. The sealed ampoule was then put into a covered  $-20^{\circ}$  bath of glycol-water for at least 15 min and allowed to equilibrate in the dark. The seal was broken with the aid of a teflon covered stirring bar contained within the ampoule and the ampoule inverted to let the chlorine monoxide solution run into the cyclohexene at  $-20^{\circ}$  in the dark. The solution became cloudy and colorless as soon as the chlorine monoxide came in contact with the cyclohexene. The ampoules were kept at  $-20^{\circ}$  prior to analysis. Undegassed ampoules contained atmospheric amounts of oxygen.

#### Analysis

Analysis of the products from the reaction of chlorine monoxide with cyclohexene was carried out by gas chromatography (g.l.p.c.) on an Aerograph Model 1520-B chromatograph utilizing the flame ionization detector and matrix programmer. All of the products, with the exception of 4, were analyzed using a 10 ft 0.125 in. polypropylene glycol (PPG) column (40–145°). By use of an internal standard, "Freon 112", the absolute amounts of products 1-3 were determined using calibration plots of area ratios vs. mol ratio for the standard vs. the authentic samples.

The yield of 4 was obtained relative to 3 using a 10 ft 0.125 in. NPGS column (70-200°).

The reaction mixtures containing cyclohexane with added amounts of cyclohexene were frozen with liquid nitrogen, and quenched with acidified potassium iodide solution immediately after mixing at  $-20^{\circ}$  in the dark. Analysis of the reaction mixture was done by g.l.p.c. utilizing a 10 ft 1/4 in. column packed with Apiezon N, 5%, on Chromosorb P. The analysis was carried out using a thermal conductivity detector. The analysis for cyclohexyl chloride was quantitated using an external standard, *o*-dichlorobenzene, and standard calibration curves were used to determine absolute amounts.

#### **Product Identification**

Most of the products were identified by comparing their g.l.p.c. retention times with those of authentic samples. The columns used for comparison of retention times were at least one of the columns mentioned previously (PPG and/or NPGS) and a 10 ft 0.125 in. SE-30 (Methyl) column.

Compounds 1, 3, and 5 were further identified by comparing their mass spectra with those of commercial samples. Due to their small amounts, the compounds were analyzed by an AEI MS12 mass spectrometer coupled to a Varian Aerograph series 1200 chromatograph fitted with a 10 ft 0.125 in. PPG column.

#### trans-2-Chlorocyclohexanol (2)

The compound was isolated from a reaction mixture by distillation through a spinning band column (50° at

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25 mm); the infrared spectrum displayed a strong band at  $3400 \text{ cm}^{-1}$  and was identical to that of a commercial sample and the same as reported by Stevens and Grummitt (10).

Anal. Calcd. for C<sub>6</sub>H<sub>11</sub>OCl: C, 57.37; H, 7.97. Found: C, 57.33; H, 8.01.

2,2'-Dichlorocyclohexyl Ether (4)

A reaction mixture was distilled under vacuum,  $60^{\circ}/20$  mm. The residue was subjected to column chromatography on silica gel (chloroform-benzene).

The fraction containing mainly (4) was purified by vacuum distillation by collecting the fraction that distilled at  $90-91^{\circ}/0.1$  mm. Analysis by g.l.p.c. showed the fraction to contain at least three compounds. The chromatogram showed a major sharp peak followed by a smaller broad peak composed of at least two compounds in the ratio of 7:3, respectively. Since four isomers of the ether are possible, it is reasonable to assume that the purified fraction of compound 4 contains these isomers.

Anal. Calcd. for  $C_{12}H_{20}OCl_2$ : C, 57.37; H, 7.97. Found: C, 57.24; H, 7.79.

Also consistent with the formula was the mass spectrum. The exact mass by a mass spectrum was 250.0891 (Calcd. 250.0892) and a pattern of three peaks in the ratio of 9:6:1 at the parent peak was indicative of the presence of two atoms of chlorine in the molecule. The infrared spectrum of compound 4 shows a broad ether band at  $1095 \text{ cm}^{-1}$  and no carbonyl or alcohol bands. The n.m.r. spectrum shows two broad multiplets at 6.3 and 8.2 in the ratio of 1:4, respectively. This is comparable to the n.m.r. spectrum of *trans*-2-chlorocyclohexanol which shows peaks at 5.65, 6.4, and 8.4 in the ratio of 1:2:8, respectively.

### 2-Chlorocyclohexanone (6)

An authentic sample of the material displayed the same retention times as a sample obtained from the reaction. The material in the reaction mixture was consumed (g.l.p.c. analysis) when the reaction mixture was shaken with an acidified solution of 2,4-dinitrophenylhydrazine. An infrared spectrum of the reaction mixture displayed an absorption band at  $1720 \text{ cm}^{-1}$ , consistent with that of 6.

# Other products

Two products in the reaction mixture of cyclohexene – chlorine monoxide were identified as 2-cyclohexenone (8) and 2-cyclohexenol (9) by comparison of retention times with commercial samples. These compounds (8 and 9) were always present when the mixture was analyzed, although their areas varied with cyclohexene concentrations. The areas of these two peaks were greatest for undegassed reactions. The peaks also increased if the reaction mixture remained at room temperature for any period of time.

Gas-liquid partition chromatographic retention times of authentic materials were used to establish the absence of *cis*-2-chlorocyclohexanol, cyclohexanol, cyclohexene oxide, *cis*-1,2-dichlorocyclohexane, and chlorocyclohexane.

### Hypochlorous Acid Reaction

The reaction of hypochlorous acid with cyclohexene was carried out in a degassed ampoule with a tenfold excess of cyclohexene in carbon tetrachloride and reacted via a break seal as described earlier. The ampoules were put in a  $-20^{\circ}$  bath and shaken vigorously during the course of reaction. Vigorous shaking of the mixture prevented the aqueous solution from freezing during reaction. After two minutes, 25% of the hypochlorous acid still remained and after five minutes the reaction was at least 95% complete. After 10 min of shaking at  $-20^{\circ}$  in the dark, the reaction mixture showed less than one percent titer (greater than 99% reaction). Analysis of the mixture by g.l.p.c. showed the presence of a number of the products present in the cyclohexene - chlorine monoxide reaction. The main product was the chlorohydrin (2). Compounds 3 and 4 were present in equal amounts (about 25% of 2) and compounds 1 and 5 were also present; together they made up about 10% of the total. The ratio of 1:5 was about 2:1.

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