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Kinetics, Products, and Stereochemistry of the Reaction of Chlorine Atoms with *cis*- and *trans*-2-Butene in 10−700 Torr of N_2 or N_2/O_2 Diluent at 297 K

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The reactions of Cl atoms with *cis*- and *trans*-2-butene have been studied using FTIR and GC analyses. The rate constant of the reaction was measured using the relative rate technique. Rate constants for the cis and trans isomers are indistinguishable over the pressure range 10−900 Torr of N_2 or air and agree well with previous measurements at 760 Torr. Product yields for the reaction of *cis*-2-butene with Cl in N_2 at 700 Torr are *meso*-2,3-dichlorobutane (47%), DL-2,3-dichlorobutane (18%), 3-chloro-1-butene (13%), *cis*-1-chloro-2-butene (13%), *trans*-1-chloro-2-butene (2%), and *trans*-2-butene (8%). The yields of these products depend on the total pressure. For *trans*-2-butene, the product yields are as follows: *meso*-2,3-dichlorobutane (48%), DL-2,3-dichlorobutane (17%), 3-chloro-1-butene (12%), *cis*-1-chloro-2-butene (2%), *trans*-1-chloro-2-butene (16%), and *cis*-2-butene (2%). The products are formed via addition, addition−elimination from a chemically activated adduct, and abstraction reactions. These reactions form (1) the stabilized 3-chloro-2-butyl radical, (2) the chemically activated 3-chloro-2-butyl radical, and (3) the methylallyl radical. These radicals subsequently react with Cl_2 to form the products via a proposed chemical mechanism, which is discussed herein. This is the first detailed study of stereochemical effects on the products of a gas-phase Cl+olefin reaction. FTIR spectra (0.25 cm^{-1} resolution) of *meso*- and DL-2,3-dichlorobutane are presented. The relative rate technique was used (at 900 Torr and 297 K) to measure: $k(Cl + \text{3-chloro-1-butene}) = (2.1 \pm 0.4) \times 10^{-10}$, $k(Cl + \text{1-chloro-2-butene}) = (2.2 \pm 0.4) \times 10^{-10}$, and $k(Cl + \text{2,3-dichlorobutane}) = (1.1 \pm 0.2) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

1. Introduction

The kinetics of the reaction of 2-butene with Cl atoms has been studied previously using relative rate techniques at ambient temperature and pressure.[1−3] The importance of this reaction to the atmospheric photochemistry of coastal regions is discussed in these references and will not be presented here. Only one of these papers[3] examined products formed, and those experiments were performed in air.

The research presented herein describes the gas-phase chemistry of the reaction of Cl atoms with *cis*- and *trans*-2-butene in either nitrogen or air/oxygen diluent. Experiments are performed to measure the rate constants of these reactions as a function of pressure at 297 ± 1 K and to identify the products formed. Particular emphasis is placed on determining the yields of the stereoisomers. In nitrogen diluent, these stereoisomers include *cis*- and *trans*-1-chloro-2-butene (crotyl chloride) and the meso and DL (racemic) forms of 2,3-dichlorobutane. Chlorine-atom-catalyzed isomerization of the reactant cis/trans butenes also occurs, as has been observed in similar addition reactions of iodine atoms to cis and trans olefins (see refs 4 and 5 and citations therein). In the presence of oxygen, the products named above (with the exception of the Cl-catalyzed isomerization product) were eliminated and replaced with oxygenated organic species. A heterogeneous reaction was observed between molecular chlorine and the 2-butenes in the dark. The rate constant and products of this dark reaction were determined, and the product data are compared to data obtained in liquid-phase measurements.[6]

To our knowledge, this is the first examination of the effect of stereochemistry on the products formed during a gas-phase reaction of an olefin with chlorine atoms. $CH_3CH{=}CHCH_3$ (2-butene) is the smallest olefin that possesses all of the possible types of reactions that can occur in larger olefin molecules and is, therefore, well suited to gaining an understanding of these types of stereochemical processes.

2. Experimental Section

Measurements were carried out in two different reactor/analysis systems, both operated at ambient temperature. One system consisted of a spherical (500 cm^3) Pyrex reactor. The concentrations of reactants and products in this reactor were measured by gas chromatography. The second system was an FTIR smog-chamber (140 L) reactor. These two systems are discussed separately in the following sections.

2.1. FTIR Smog Chamber System. Experiments were performed to measure k_2/k_1, and the products formed in 10, 50, or 700 Torr of N_2 or air/O_2 diluent at 296 K using a cylindrical, 140 L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer. The apparatus and techniques are described in

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detail elsewhere.[7] The reactor was surrounded by fluorescent blacklamps (GE F15T8-BL), which were used to generate Cl atoms by photolysis of molecular chlorine:

$$Cl_2 + h\upsilon \rightarrow 2Cl$$

$$Cl + C_3H_6 \rightarrow \text{products} \tag{1}$$

$$Cl + \textit{trans}\text{-2-}C_4H_8 \rightarrow \text{products} \tag{2a}$$

$$Cl + \textit{cis}\text{-2-}C_4H_8 \rightarrow \text{products} \tag{2b}$$

Reactant mixtures were prepared using calibrated volumes on an external gas handling manifold and flushed into the chamber with the diluent gas. Reactant and product compounds were monitored by FTIR spectroscopy using an infrared path length of 27.1 m and a resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 co-added interferograms. All reactants were obtained from commercial sources at purities >99.9%. The reactants were subjected to freeze/thaw cycles to remove impurities. Rate constant measurements were carried out using propylene as the reference compound. Product measurements were performed using 2-butene/Cl_2 mixtures in N_2 or N_2/O_2 diluent. Propylene was used in the FTIR relative rate experiments because its IR spectrum has structured features that are convenient to analyze. However, the use of propylene as the reference compound in relative rate studies conducted over a range of total pressure is complicated by the pressure dependence of the Cl + propylene reaction.

Calibration of the FTIR absorption signal requires pure samples of the reactants and products. For most of the critical species, pure compounds were available (purity >95%). However, for two important species, the stereoisomers were not available in pure form. These compounds were *meso*- and DL-2,3-dichlorobutane, and *cis*- and *trans*-1-chloro-2-butene. These species could only be purchased as mixtures of the two isomers, whose relative concentrations could be determined by the GC instrument. For the 2,3-dichlorobutane species, two commercial samples were purchased, which had very different meso/DL ratios as measured by GC (see section 2.2). This permitted a deconvolution of the two spectra and a calibration of the two individual stereoisomers in the FTIR measurements (see spectra in Appendix A). For 1-chloro-2-butene, samples with significantly different cis/trans ratios were not available, and no deconvolution was possible. However, the trans isomer represented ~85% of the calibration sample of 1-chloro-2-butene as measured by GC, allowing a reasonable calibration for the trans isomer. The cis isomer could not be calibrated, and its IR spectrum remains unknown.

2.2. GC Reactor System. The relative rate experiments using GC detection were carried out in a spherical, Pyrex (500 cm^3) reactor. The kinetics and product studies were performed using $Cl_2/CH_4/C_3H_8/2\text{-}C_4H_8$ mixtures in N_2 (UHP) diluent (all purities >99.9%; freeze thaw cycles were performed on the 2-butene and Cl_2 reactants). Methane was used for internal calibration of the GC analysis because it is essentially unreactive toward Cl ($k = 1 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}) relative to the other hydrocarbons in the mixture. Propane was used as the reference compound in the GC relative rate experiments because it is convenient to measure using the GC technique and because k_3 is well established and independent of pressure.

$$Cl + C_3H_8 \rightarrow \text{products} \tag{3}$$

Propane was not an optimal choice as reference for the FTIR experiments because its IR spectrum is broader, less intense, less structured, and hence more difficult to quantify than propylene.

Each reactant sample was mixed in the reactor prior to irradiation. Chlorine atoms were generated by irradiation with UV light using a single Sylvania F6T5 BLB fluorescent lamp. After a chosen irradiation time, a portion of the contents of the reactor was removed and analyzed by gas chromatography. The mixture was then irradiated for additional times, and additional analyses were performed. The irradiation was not uniform in the GC experiments (unlike the FTIR experiments) because a single fluorescent bulb placed beside the reactor was used. Measurements of the rates of reaction of Cl with the product molecules (1-chloro-2-butene, 2,3-dichlorobutane, and 3-chloro-1-butene) were also performed relative to propane in this reactor to enable correction of the product yields from reaction 2 for secondary consumption by Cl (see Appendix B).

The gas chromatograph was a HP 5890 GC/FID equipped with a 30 m, 320μ, DB-1 capillary column with 5 μ coating. The temperature program used in the analyses began with an initial 6 min period at 35 °C followed by a temperature ramp of 8 °C/min to 180 °C. The He carrier flow rate was ~1.8 cm^3/min. At the stated conditions, this column separates to the baseline the cis (retention time = 4.75 min) and trans (4.37 min) isomers of 2-butene and the meso (18.04 min) and DL (18.63 min) stereoisomers of 2,3-dichlorobutane. It also provides near baseline separation of the cis (14.43 min) and trans (14.28 min) isomers of 1-chloro-2-butene. This column separates compounds of like structure on the basis of boiling point. Thus, *trans*-2-butene (bp = 274.2 K) elutes before the cis isomer (bp = 276.8 K), as verified by pure samples of the two isomers. The boiling points of the two isomers of 1-chloro-2-butene are not available, to our knowledge, but the individual isomers were identified on the basis of their relative signal strengths in a commercial 1-chloro-2-butene sample from TCI America, which the supplier stated was ~86% trans and ~13% cis. Samples of 2,3-dichlorobutane for calibration of the GC and FTIR were purchased from both TCI America and Pfaltz and Bauer. These samples were unknown mixtures of the meso and DL components. The retention times of the individual 2,3-dichlorobutane stereoisomers were identified on the basis of the known boiling points of these isomers. The boiling points[8] are as follows: meso (322.7 K); DL (326.3 K). Therefore, the meso isomer will elute before the DL isomer on this DB1 column. Based on the GC analyses, the compositions of the TCI America and of the Pfaltz and Bauer samples were [74% meso]/[26% DL] and [57% meso]/[43% DL], respectively, permitting deconvolution of the FTIR spectra.

3. Results and Discussion

3.1. Dark Chemistry. The dark chemistry [reactions 4a,b and 5] was studied in some detail because it can interfere with the evaluation of the chemistry occurring during irradiation. It is well-established that Cl_2 reacts in the dark with 2-butene in the liquid phase.[6,8] During the current experiments, gaseous Cl_2 was mixed with *cis*- or *trans*-2-butene in either the FTIR or the GC reactors and allowed to stand in the dark for periods of up to several hours. Experiments in both reactors verified that a dark reaction does occur between these reactants. Table 1 presents the initial conditions and the product yields measured in a series of studies of the dark reaction in each reactor. Rate constants determined for this bimolecular reaction are shown in the last column. The rate constants vary from (2.4 to 11) × 10^{-21} cm^3 $molecule^{-1}$ s^{-1} in the GC experiments and from (1.4

TABLE 1: Product Yields and Rate Constants from the Dark Reaction of Molecular Chlorine with 2-Butene

							2,3-dichlorobutane %[d]					
	type	$2\text{-}C_4H_8$[a] mTorr	Cl_2 mTorr	P (N_2) Torr	$\sum C$[b]	$[C]/[C_0]$	meso[c]	DL[c]	1-Cl-2-butene %[d]	3-Cl-1-butene %[d]	HCl %[d]	k_4 cm^3 molecule^{-1} s^{-1}
A	GC-trans	35[4]	115	900	100	0.94−0.58	86(7)	<0.8	<0.3	14(3)		2.4×10^{-21}
B	GC-cis	35[1]	40	900	91	0.87	<1.3	77	<0.5	14		3.6×10^{-21}
C	GC-cis	90[4]	113	900	92	0.93−0.78	1(0.5)	74(5)	<0.1	17(2)		4.2×10^{-21}
D	GC-cis	34[4]	404	900	92	0.93−0.55	<0.6	77(5)	<0.2	14.5(3)		3.2×10^{-21}
E	GC-cis	69[4]	116	900	96	0.93−0.71	1(0.5)	72(7)	<0.3	23(3)		1.1×10^{-20}
F	FTIR-trans	223[4]	220	700	105	0.97−0.946	93(4)	3.9(2)	<0.6	8.3(2.5)	8.5(1)	4.7×10^{-21}
G	FTIR-trans	223[6]	236	700	99	0.98−0.89	88(5)	<0.8	<1	11(1.5)	12(2)	1.4×10^{-21}
H	FTIR-trans	68[2]	2000	700	95	0.78−0.6	71(3.5)	7.6(2.5)	6(1.2)	10.7(1.3)		2.1×10^{-21}
I	FTIR-cis	78[2]	2000	700	100	0.79−0.63	<3	85	N/A	15(1.5)		2.3×10^{-21}
J	liq-trans[e]						98	<0.3	<0.2	2		
K	liq-cis[e]						<1	97	<0.2	3		

[a] Partial pressure of 2-butene in mixture [number of data points taken under the stated conditions shown in brackets]. [b] Sum of the molar hydrocarbon product yields. [c] meso = non-optically active stereoisomer; DL = racemic stereoisomer. [d] Mole percent product (per mole of 2-butene consumed) − estimated error in parentheses. [e] Liquid experiments from ref 6 carried out under O_2; see text.

to 4.7) × 10^{-21} cm^3 molecule^{-1} s^{-1} in the FTIR reactor. The fact that the rate constant varies by factors of 3−4 upon repeat measurements in each reactor indicates that the reaction proceeds predominantly, perhaps exclusively, via a heterogeneous mechanism. In calculating the rate constants, no correction was made for consumption of Cl_2. Typically this consumption would result in a correction of less than 15%. Because the rate constants vary by factors of up to 4, such a correction was deemed unnecessary.

$$trans\text{-}2\text{-}C_4H_8 + Cl_2 = meso\text{-}2,3\text{-dichlorobutane} \quad (4a)$$

$$cis\text{-}2\text{-}C_4H_8 + Cl_2 = \text{DL-}2,3\text{-dichlorobutane} \quad (4b)$$

$$cis\text{-}/trans\text{-}2\text{-}C_4H_8 + Cl_2 = 3\text{-chloro-}1\text{-butene} + HCl \quad (5)$$

The GC experiments (data sets A−E) show that three products are formed. *trans*-2-Butene forms *meso*-2,3-dichlorobutane with no measurable production of the DL stereoisomer. *cis*-2-Butene forms the DL isomer with no meso formation. Both 2-butene isomers form 3-chloro-1-butene with ∼15% yield. The GC experiment with the highest rate constant (data set E) forms a somewhat higher yield of 3-chloro-1-butene, although the difference is only modestly outside of the estimated combined experimental error and may not be significant. All of the data sets in the GC reactor have excellent carbon balances of 90−100%. No changes in product yields were observed upon variation of the initial *cis*-2-butene (35−90 mTorr) and chlorine (40−400 mTorr) partial pressures. 1-Chloro-2-butene formation was not observed in these experiments.

The product yields obtained from *trans*-2-butene at ∼230 mTorr of both Cl_2 and butene in the FTIR reactor (data sets F and G) are similar to those from the GC reactor, although the 3-chloro-1-butene yield is somewhat lower and a small yield of DL-2,3-dichlorobutane from the trans isomer was observed, which was of marginal significance (4 ± 2%). The carbon balances for these FTIR data sets were 99−105%.

Table 1 (data sets J and K) shows results from liquid-phase experiments carried out in the dark in the presence of O_2 to suppress Cl chain propagation, which was observed to occur even in the absence of irradiation in those experiments.[6] The products formed are identical to those in the current gas-phase experiments. *meso*-2,3-Dichlorobutane is the only isomer formed from *trans*-2-butene, while DL-2,3-dichlorobutane is the only isomer formed from *cis*-2-butene. This agreement provides support for the identification of the stereoisomers in the present GC analyses, which were based on boiling point. The only major difference between the gaseous and liquid experiments is in the yield of 3-chloro-1-butene, which is much smaller in the liquid data. In the liquid-phase experiments, consumption of 2-butene was not measured directly. The yields were obtained using the sum of the products as a measure of the butene consumption.

For *trans*-2-butene reaction at a higher Cl_2 partial pressure (2 Torr, data set H in Table 1), 1-chloro-2-butene is formed in contrast to the results at lower Cl_2 partial pressure. Whether this is because of a small light leak during this individual experiment or because of dark chain propagation at high Cl_2 is not known. However, Poutsma did observe some chain propagation in the absence of irradiation in his liquid experiments, which was the reason why those experiments were performed in the presence of the radical scavenger O_2.[6]

Data sets F and G show formation of HCl during the reaction with *trans*-2-butene even though there is no evidence of chain propagation. If chain propagation were occurring, *trans*-1-chloro-2-butene would be formed, but no *trans*-1-chloro-2-butene is observed in the products. The HCl yield is equal to the yield of 3-chloro-1-butene to within experimental error. It is likely that 3-chloro-1-butene is also formed by molecular reaction 5 of Cl_2 with the 2-butenes. The fact that the yield of this species varies somewhat between reactors is consistent with the hypothesis that it too is a heterogeneous reaction product.

Figure 1 presents plots of the concentrations of *cis*-2-butene and propane in the GC reactor (both were present in the reactant mixture during this GC experiment) as functions of time after mixing in the dark. The data in this plot are from run D (GC reactor) in Table 1. The slope of the *cis*-2-butene curve gives the rate constant for reaction 4b [3.2 × 10^{-21} cm^3 molecule^{-1} s^{-1}] in this specific data set. Propane is not consumed to within experimental error, providing additional verification that the dark reaction does not have any measurable Cl chain propagation in the GC reactor (if Cl atoms were present during the dark reaction, propane would be consumed).

The conventional explanation for the observation that *trans*-2-butene forms only meso isomer while cis forms solely DL in the liquid involves the formation of a bridged, positively charged, ionic intermediate. According to this hypothesis, the positively charged intermediate maintains the stereo-orientation of the initial 2-butene isomer and subsequently reacts with a Cl^- anion to form either the *meso*- or the DL-2,3-dichlorobutane product. This mechanism (often involving bromination rather than chlorination) is presented in many organic chemistry text books (e.g., ref 9) and has been discussed in an early paper on the topic.[8] The observation of similar product yields in the gas-phase reaction where an ionic mechanism as described above

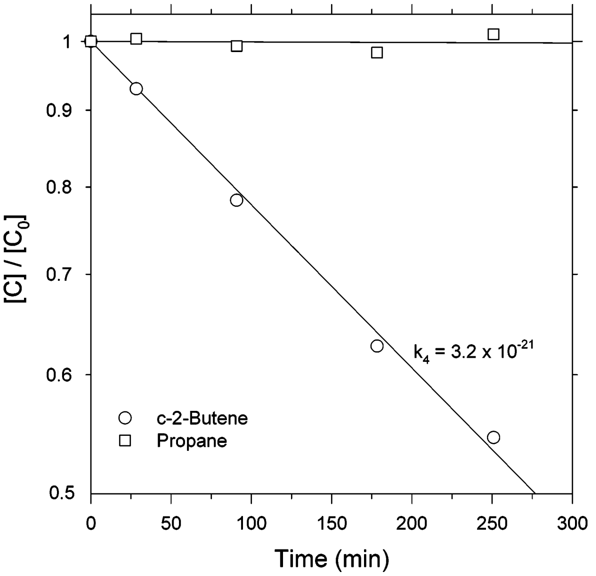
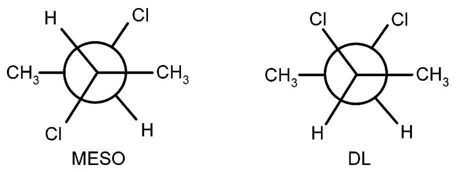


Figure 1. Dark reaction of a *cis*-2-butene, propane, Cl_2 mixture in 900 Torr of N_2 in the GC reactor. See data set D in Table 1. $k_4 = 3.2 \times 10^{-21}$ cm^3 $molecule^{-1}$ s^{-1}. $[C]/[C_0]$ is plotted on a log scale.

seems unlikely to occur suggests that this mechanism may not be the only possible explanation for the observed stereochemistry of the products. In fact, Poutsma[6] (see page 2177 of this reference) suggests that the reaction in his liquid experiments occurs via a “rather tight ion pair”.

To explain the stereo-orientation of the product 2,3-dichlorobutane in the current experiments, the stereoconfigurations of the meso and DL isomers must be examined. Diagrams of the two isomers are presented below. Each diagram shows a possible conformation of one stereoisomer in which the methyl groups are anti (i.e., trans) with respect to one another. Other conformations are obtained by internal rotation of the molecule about the central C−C bond (e.g., another form of the DL isomer, which has methyl groups syn (i.e., cis) and Cl atoms nearly anti). Careful examination shows that these two isomers cannot be transformed into one another by simple rotation about the central C−C bond and are in fact separate chemical compounds with differing boiling points as discussed above. The racemic DL mixture contains equal amounts of the D and L isomers, which are non-superimposable mirror images of one another formed by reflection through a plane. Only one of the DL isomers is shown.



It would seem that the Cl_2 molecule must approach the C═C double bond in 2-butene with the Cl−Cl bond oriented nearly perpendicularly to the C═C double bond during the surface-catalyzed dark reaction. This would allow the Cl_2 molecule to overlap with the π electron orbitals both above and below the plane of the 4 carbon atoms. The above diagrams show that this would yield a meso isomer from *trans*-2-butene with one chlorine on each side of the plane formed by the 4 carbon atoms. If the Cl_2 approached parallel to the C═C double bond and interacted with the π orbital located either above or below the plane, the opposite stereo-orientation of the products would be observed. Both chlorines would be on the same side of the plane of the carbon atoms (i.e., DL from *trans*-2-butene) contrary to the experimental data. These data cannot determine which reactant species is adsorbed on the surface during the heterogeneous reaction.

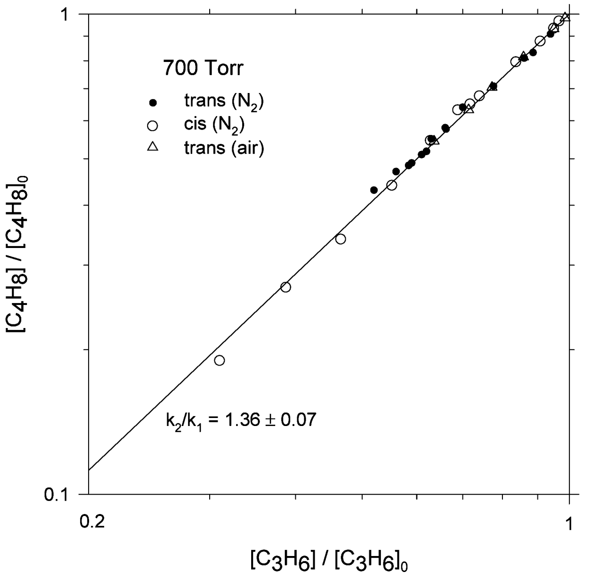
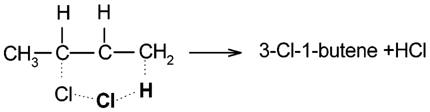


Figure 2. Plot of the consumption of *cis*- and *trans*-2-butene relative to that of propylene in the FTIR reactor for irradiated mixtures of 2-butene, propylene, and chlorine with nitrogen or air as diluent at 700 Torr. The axes are plotted as log. The slope represents the rate constant ratio k_2/k_1. Error limits are statistical only.

A possible explanation for the formation of 3-chloro-1-butene in a heterogeneous molecular reaction with Cl_2 is the formation of a six-member cyclic transition state, which would have little ring strain and could subsequently eliminate HCl to form 3-chloro-1-butene. Based on the FTIR experiments, HCl is formed with a yield equal to that of 3-chloro-1-butene during the dark reaction. The heats of reactions[10] for (4a) and (4b) [−45.7 and −46.5 kcal/mol, respectively] and (5) [−31.1 kcal/mol] are all significantly exothermic and, therefore, thermodynamically favored at ambient temperature.



3.2. Relative Rate Study of k_2(Cl+2-Butene) in 10−900 Torr of N_2 and N_2/O_2. Figure 2 presents measurements of the rate of consumption of *cis*- and *trans*-2-butene by Cl atoms [reaction 2] relative to that of the reaction of Cl with propylene [reaction 1] at 700 Torr using the FTIR reactor. Data for the reaction of Cl with both butene isomers in 700 Torr of N_2 and for the trans isomer in 700 Torr of air are plotted together in Figure 2 relative to the consumption of the propylene reference compound. To within the 5% (2σ) statistical error, all of the data at 700 Torr can be fitted by a single least-squares line, which yields a rate constant ratio $k_2/k_1 = 1.36 \pm 0.07$ (2σ). At 700 Torr, the rate constants for reaction of Cl with both *cis*- and *trans*-2-butene are indistinguishable in N_2 and air diluents. Data at 10 Torr of N_2 are presented in Figure 3 for the *cis*- and *trans*-2-butene isomers. While it is possible that the rate constants for the cis and trans isomers differ slightly at 10 Torr, the 10% difference is nearly within the sum of the statistical error limits presented in Figure 3.

Table 2 lists the rate constant ratios and rate constants from experiments at 10−900 Torr total pressure using both GC and

TABLE 2: Measured Rate Constants for Cl + 2-Butene [Reaction 2]

	isomer	method	P (Torr)	reference	diluent	relative rate ratio	k_2 (10^{-10} cm^3 molecule^{-1} s^{-1})
A	**trans/cis**	**FTIR**	**700**	**propylene**	**N$_2$ or air**	**1.36 (0.07)**[a]	**3.58 ± 0.23**
B	**trans**	**GC**	**900**	**propane**	**N$_2$**	**2.27 (0.22)**	**3.27 ± 0.3**
C	**cis**	**GC**	**900**	**propane**	**N$_2$**	**2.2 (0.2)**	**3.13 ± 0.3**
D	**trans**	**GC**	**50**	**propane**	**N$_2$**	**2.03 (0.2)**	**2.9 ± 0.3**
E	**cis**	**GC**	**50**	**propane**	**N$_2$**	**1.87 (0.2)**	**2.7 ± 0.3**
F	**trans**	**FTIR**	**10**	**propylene**	**N$_2$**	**3.6 (0.18)**[b]	**3.1 ± 0.16**
G	**cis**	**FTIR**	**10**	**propylene**	**N$_2$**	**4.0 (0.2)**[b]	**3.5 ± 0.18**
H	trans	FTIR	700	propylene	air	1.54 (0.12)[c]	4.0 ± 0.3
I	trans	FTIR	760	propylene	N$_2$ or air	1.3 (0.22)[d]	3.42 ± 0.6
J	trans	GC	760	*n*-heptane	N$_2$ or air	0.834 (0.1)[e]	3.4 ± 0.6
K	cis	GC	760	*n*-heptane	N$_2$ or air	1.02 (0.18)[e]	3.76 ± 0.84

[a] See data in Figure 2. All values of k_2 with propylene reference are calculated using $k_1 = 2.63 \times 10^{-10}$ at 700 Torr and 8.7×10^{-11} at 10 Torr; those with propane reference are calculated using $k_3 = 1.43 \times 10^{-10}$ at both pressures. Data in bold type are from current experiments. Uncertainties (shown in parentheses) for current experiments are statistical (2σ) only. [b] See Figure 3. [c] Reference 3. [d] Reference 1. Reference rate constant corrected to 2.63×10^{-10} (see text). [e] Reference 2.

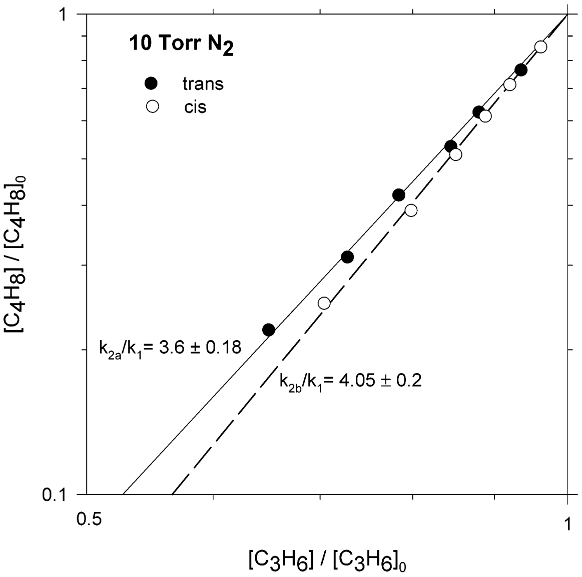


Figure 3. Plot of the consumption of *cis*- and *trans*-2-butene relative to that of propylene in the FTIR reactor for irradiated mixtures of 2-butene, propylene, and chlorine with nitrogen as diluent at 10 Torr. The axes are plotted as log. The slope represents the rate constant ratio k_2/k_1. Error limits are statistical only.

FTIR reactors [data from the present work are shown in bold type (data sets A−G)]. Table 2 also contains the ratios and rate constants determined by three other research groups. In calculating k_2 from the relative rate data, the rate constants for the reference compounds propane and propylene (at ~700 Torr) are those suggested by Orlando et al.[3] [propane ($k_3 = 1.43 \times 10^{-10}$) and propylene ($k_1 = 2.63 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1})]. The stated value for k_1 increases the calculated value of k_2 in ref 1 by about 10% (data set I in Table 2). These authors apparently used a value for k_1 ($=2.3 \times 10^{-10}$) that appears to include only the addition reaction rather than the overall rate constant that has an abstraction component as well. Determining the rate constant k_2 from the value of k_2/k_1 at 10 Torr in the FTIR reactor requires a determination of the pressure-dependent rate constant for propylene, k_1, at 10 Torr. In ref 11 (see Table 1 of that reference), measurements of k_1 relative to ethane were made at 10.2 Torr ($k_1/k_{\text{ethane}} = 1.5$) and at 700 Torr ($k_1/k_{\text{ethane}} = 4.54$). Based on these data and the fact that the rate constant for the reaction of Cl with ethane is independent of pressure, k_1 (700 Torr)/k_1 (10 Torr) = 4.54/1.5 = 3.03, and, therefore, k_1 (10 Torr) = 8.7×10^{-11} cm^3 molecule^{-1} s^{-1}.

The values of k_2 determined in the current study by both GC and FTIR at 700−900 Torr (data sets A, B, and C) agree to within the statistical error limits of the relative rate determinations, not including any uncertainty in the rate constants of the two reference compounds. The data obtained using both GC and FTIR techniques show that there is no statistically significant difference between the rate constants of the cis and trans isomers for $P \geq 700$ Torr. They also agree that any pressure dependence in k_2 is small over the pressure range studied (<20% between 10 and 900 Torr). This lack of pressure dependence contrasts with the factor of 3 increase in the value of k_1 as the pressure increases from 10 to 700 Torr. Propylene has fewer vibrational degrees of freedom over which to stabilize the activated complex.

All measurements of k_2 for $P \geq 700$ Torr presented in Table 2 (which were obtained using three different reference compounds in five reactors) agree well. The average of the high pressure measurements of both isomers (data sets A, B, C, H, I, J, and K) yields a rate constant of $(3.5 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, in which the error represents statistical uncertainty (2σ) only. This should also provide a reasonable estimate of the overall uncertainty including that of the reference compounds because the rate constants have been obtained using three separate reference species.

Poutsma[6] conducted liquid-phase relative rate experiments measuring the reactivity of Cl atoms toward 2-butene using cyclohexane as a reference. Based on Poutsma's published relative rate ratio (k[2-butene]/k[cyclohexane] = 1.3, see Table 10 of ref 6) and the currently accepted rate of the reaction of cyclohexane with Cl in the gas phase[12] (3.1×10^{-10}), we find $k_2 = 4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. This result is in excellent agreement with the results from the gas-phase experiments listed in Table 2.

3.3. Products Observed Following UV Irradiation of Cl$_2$/2-Butene Mixtures in N$_2$ Diluent. Figure 4 presents the partial pressures of the products formed from reaction 2a as a function of *trans*-2-butene consumed at a total pressure of 700 Torr (N$_2$) in the FTIR reactor. The partial pressures of the products have been corrected for secondary consumption by Cl atoms using rate constants determined in the current experiments described in Appendix B. After these corrections were applied, the concentrations of the four major products (*meso* and DL)-2,3-dichlorobutane, 1-chloro-2-butene, and 3-chloro-1-butene increase linearly with consumption of *trans*-2-butene (over the range 30−90%), showing that they are primary products. The lines through the data in Figure 4 are linear least-squares fits,

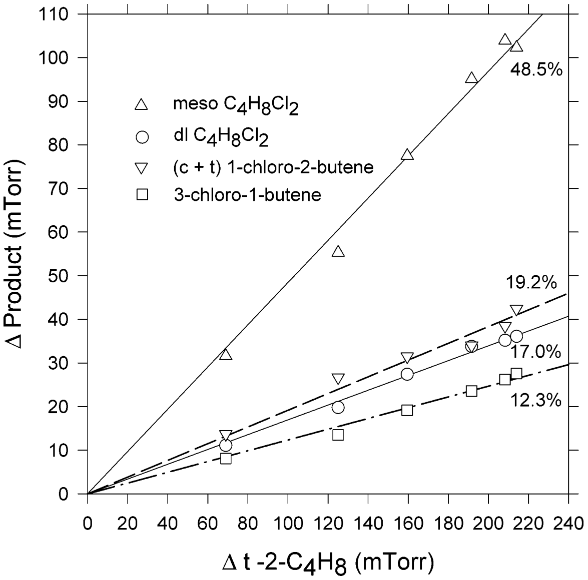


Figure 4. Partial pressures of the major products plotted as a function of the partial pressure of *trans*-2-butene consumed for reaction of *trans*-2-butene with Cl at 700 Torr in the FTIR reactor (see data set I in Table 3). Partial pressures of the products have been corrected for secondary consumption by Cl. Also shown are the percentage yields of the products (mole of product/mole of *trans*-2-butene consumed).

which give the molar yields indicated on the figure. The sum of the yields of these four products is 97% in this experiment.

Product yields measured in both reactors are shown in Table 3 (*trans*-2-butene) and Table 4 (*cis*-2-butene) for the two initial reactant partial pressures investigated. No significant difference in the product yields was observed for two initial reactant partial pressures at the same total pressure (e.g., in Table 3, compare data sets C and D to H and I, and G to L). Experiments were also performed in which the photolysis light intensity during FTIR experiments was varied to change the steady-state Cl atom density. No difference in product yields was observed for average [Cl] densities of 3.5 and 16 × 10^7 cm^{-3} at one initial condition [*cis*-2-butene = Cl_2 = 225 mTorr; N_2 = 700 Torr].

Each of the reactors has limitations with respect to the measurement of the yields of specific species, and these limitations will be discussed first. When experiments were performed in the GC reactor, significant dark reaction takes place quickly (in <2 min) during the mixing of the reactants for reasons that are unknown. Thus, immediately after reactant mixing, the non-irradiated mixture contains some 2,3-dichlorobutane (only meso when using *trans*-2-butene and DL when using the cis isomer) and a lesser amount of 3-chloro-1-butene. This effect is measured by carrying out a GC analysis prior to irradiation. A second source of dark reaction products results from the fact that the GC analysis procedure takes ~30 min to complete. Therefore, between irradiations in this reactor and the subsequent GC analyses, the slower dark reaction described in section 3.1 also occurs. Approximate corrections for these two dark reaction sources have been made by subtracting an estimate of the dark yield prior to calculating the product yields formed during irradiation. These corrections are particularly difficult to quantify for the 2,3-dichlorobutane isomers because the dark yields are much larger and can approach 60% of the species yield during irradiation. Because of this, the yield of *meso*-2,3-dichlorobutane from *trans*-2-butene irradiation experiments and the yield of DL from *cis*-2-butene can have large error limits, and in some data sets not even a rough estimate of the yield is possible. No 1-chloro-2-butene is formed during mixing or subsequent dark reaction, and the isomeric yields of this species following UV irradiation can be measured accurately by GC.

The FTIR reactor produces no mixing-related dark reaction, and acquiring a FTIR spectrum takes only 2 min. Therefore, dark-reaction effects on product measurements are negligible in the FTIR experiments, and the partial pressures of 3-chloro-1-butene and *meso*- and DL-2,3-dichlorobutane can be measured accurately. However, as described in the Experimental Section, the cis isomer of 1-chloro-2-butene cannot be quantified because this isomer is not available commercially. Using both GC and FTIR measurements provides the yields of all isomers of the product species in N_2 diluent for reaction 2.

In Tables 3 and 4, one product, acetyl chloride (CH_3COCl), results from reactions occurring in the presence of O_2, as will be discussed later. It is apparent that varying yields of acetyl chloride are present in the FTIR experiments with N_2 diluent. This indicates that there is a measurable O_2 contamination in

TABLE 3: Product Yields Observed Following the UV Irradiation of Cl_2/*trans*-2-Butene/N_2 Mixtures

		trans-2-C_4H_8[a] mTorr	Cl_2 mTorr	*P* (N_2) Torr	∑*C*[b] %	$[C_4H_8]/[C_4H_8]_0$	*cis*-2-C_4H_8 %[c]	2,3-dichloro-butane %[c] meso[d]	2,3-dichloro-butane %[c] DL[d]	1-Cl-2-butene %[c] cis	1-Cl-2-butene %[c] trans	3-Cl-1-butene %[c]	HCl %[c]	CH_3COCl %[c]
A	GC	76[8]	73	900		0.85−0.39	0.6(0.3)	37(10)	16(2)	2.5(0.7)	14(3)	8.9(1.7)		<1.0
B	GC	66[3]	75	50		0.66−0.34	4.1(0.5)		12(0.6)	2.6(0.6)	15(2.6)	10.4(1)		<1.0
C	FTIR	76[2]	74	700	95	0.7−0.5	<4	47(5)	17(2)	19.6(1)[e]		11(1.5)	29(5)	<0.1
								50[f]	16.4[f]	2[f]	15.2[f]	11.6[f]		
D	FTIR	76[4]	75	700	92	0.78−0.26	<4	46(5)	17(2)	18.4(2)		10.6(2)	31(3)	0.3
					93		2.5(0.5)[f]	45[f]	16[f]	1.8[f]	16.2[f]	11.7[f]		
E	FTIR	74[4]	74	700	61	0.8−0.3		39(4)	13(2)	4.7(2)		4(2)		5.6
F	FTIR	73[2]	74	50	77	0.77, 0.58	<4	38(4)	14(2)	14(3)		11(2)		1.1
					83		5(1)[f]	41[f]	12.5[f]	1.8[f]	12.6[f]	10[f]		
G	FTIR	76[2]	76	10	90	0.75, 0.62	12(5)	33(4)	12(1.5)	19.1(2)		14(2)	24(5)	0.6
										3.5[f]	20[f]			
H	FTIR	228[6]	228	700	93	0.7−0.2		48(7)	17(2.5)	17.4(1.7)		11(1.4)	27(5)	0.2
I	FTIR[g]	238[6]	265	700	97	0.7−0.1		48.5(5)	17(1.5)	19.2(2.5)		12.3(1.5)	25(5)	0.2
L	FTIR	222[7]	225	10	98	0.89−0.36	12(3)	35(3)	12(2)	23(2)		16(2)		0.4
M	liq[h]							57.2	16.5		20.6[i]	5.5		

[a] Partial pressure of 2-butene in mixture [number of data points taken under the stated conditions shown in brackets]. [b] Sum of the molar hydrocarbon product yields. [c] Mole percent product (per mole of 2-butene consumed) − estimated error in parentheses. [d] meso = non-optically active stereoisomer; DL = racemic stereoisomer. [e] Only the sum (cis+trans) could be measured by FTIR (see text). [f] Measured by GC in a sample taken from FTIR chamber at maximum butene consumption (see text). [g] Data plotted in Figure 4. [h] Experiments in pure liquid 2-butene with irradiation by sun lamps (see Table 1 in ref 6). Consumption of butene was not measured in these experiments, and the percentages are calculated from the sum of the product concentrations. [i] Cis isomer not measured directly.

TABLE 4: Product Yields Observed Following the UV Irradiation of Cl_2/*cis*-2-Butene/N_2 Mixtures

		cis-2-C_4H_8[a] mTorr	Cl_2 mTorr	*P* (N_2) Torr	$\sum C$[b]	$[C_4H_8]/[C_4H_8]_0$	*trans*-2-C_4H_8 %[c]	2,3-dichloro-butane %[c]		1-Cl-2-butene %[c]		3-Cl-1-butene %[c]	HCl %[c]	CH_3COCl %[c]
								meso[d]	DL[d]	cis	trans			
A	GC	70[7]	75	900	82	0.77−0.3	1.8(0.2)	46(7)	11(4)	10(1.5)	4.5(1)	8.3(1.2)		<1
B	GC	77[5]	74	50		0.85−0.38	15(2.5)	37(5)	N/A	15.4(3)	6.4(1)	11(1.5)		<1
C	FTIR	74[4]	75	700	95	0.9−0.5	8	46(5)	17(2)	N/A[e]		11(2)	32(4)	0.3
							7[f]	43[f]		10.8(1)[f]	2.5(0.5)[f]			
D	FTIR	74[4]	75	10	104	0.83−0.5	35	22(2)	14(2)	N/A		15(2)		0.5
							31[f]	19[f]		11.8[f]	5.8[f]			
E	FTIR	230[7]	231	700		0.65−0.2	8(1.5)	49(4)	18(1.5)	N/A		13(1.5)	26(5)	<0.1
F	FTIR	248[5]	232	700	103	0.84−0.24	8(1.5)	47(4)	20(2)	N/A		13(1.5)	28(5)	<0.1
						0.55	7.5[f]	40(6)[f]		13[f]	1.7[f]			
G	FTIR	218(3)	229	700	107	0.78−0.5	9.4	49(4)	18.6(1.5)	N/A		13(1.3)	29(5)	<0.1
							8.7[f]	45[f]		14.3[f]	2.3[f]			
H	FTIR	223[7]	220	53		0.8−0.3	18(3)	41(5)	16(2)	N/A		16(2)		0.1
I	FTIR	237[4]	220	51	110	0.9−0.54	19.6(2)	39(4)	16(1.5)	N/A		16(1.5)		0.2
						0.54	20[f]	37[f]		15.5[f]	4.3[f]			
J	FTIR	223[8]	226	10		0.84−0.4	35(4)	24(3)	10.5(1.1)	N/A		18.4(2)		0.15
K	FTIR	222(3)	226	10.7	110	0.82−0.5	36	23(2)	10.3(1)	N/A		18(2)		0.16
							32[f]	22[f]		16.5[f]	5.9[f]			
L	FTIR	223(4)	217	10	114	0.8−0.5	35(4)	23(2)	9.6(1.2)	N/A		18.5(2)		0.1
							36[f]	22[f]		19(2)[f]	8.5(1)[f]			
M	liq[g]							47.3	27.5	17.3		7.9		

[a] Partial pressure of 2-butene in mixture [number of data points taken under the stated conditions shown in brackets]. [b] Sum of the molar hydrocarbon product yields. [c] Mole percent product (per mole of 2-butene consumed) − estimated error in parentheses. [d] meso = non-optically active stereoisomer; DL = racemic stereoisomer. [e] The sum (trans + cis) could not be measured by FTIR. [f] Measured by GC using a single sample taken from the FTIR chamber (see text). [g] Experiments in pure liquid 2-butene with irradiation by sun lamps (see Table 1 in ref 6). Consumption of butene was not measured in these experiments, and the percentages are calculated from the sum of the product concentrations.

many but not all of the N_2 diluent experiments. Therefore, the effect of this unavoidable contamination on the non-oxygenated product species must be assessed. Data sets C and E in Table 3 present product yields for experiments with similar initial conditions, which have the minimum and maximum measured acetyl chloride yields, respectively. In data set C, no acetyl chloride is detected (yield <0.1%), and the carbon balance (defined as the sum of the product yields) is 95 ± 10%. In data set E, which has the highest acetyl chloride yield (5.6%), the sum of the yields of the non-oxygenated species is 61 ± 10%. Therefore, ∼40% of the products in this data set must be formed via reaction with O_2 contaminant. Comparing data set D (carbon balance = 92 ± 11%) to C shows that the presence of a small amount of acetyl chloride (0.3%) affects neither the measured individual product yields nor the carbon balance to within the measurement error. In comparing data sets C and E, it is evident that the 1-chloro-2-butene and 3-chloro-1-butene product yields are much more sensitive to O_2 contamination than is the 2,3-dichlorobutane product. The yields of 1-chloro-2-butene and 3-chloro-1-butene decrease by factors of 3−4, while the dichlorobutane yield decreases by a factor of only ∼1.2 in data set E (for explanation, see Appendix C). Based on these observations, if the acetyl chloride yield is less than ∼0.5% and/or the carbon balance is >90%, the data will not be affected by unavoidable O_2 contamination to within the typical experimental error. Even somewhat larger acetyl chloride yields could probably be tolerated without affecting the product yields greatly.

As discussed above, the concentration of *cis*-1-chloro-2-butene could not be measured by FTIR. To measure the individual yields of both the cis and the trans isomers in selected experiments, a gas sample was withdrawn from the FTIR reactor into a Pyrex transfer flask at the point of maximum butene consumption and analyzed by the GC instrument. Where available, the results of these GC analyses are included in Tables 3 and 4. This method provides a measurement of the partial pressures of the 1-chloro-2-butene isomers in the FTIR reactor because neither dark formation nor consumption of this compound occurs in the transfer flask. The other compounds (2,3-dichorobutane, 3-chloro-1-butene, and the isomerized 2-butene) can also be measured by GC. However, it is possible that dark reaction could affect the measured yield of 2,3-dichlorobutane and 3-chloro-1-butene to a variable extent in the transfer flask during the time elapsed (∼30 min) between sampling and injection into the GC.

Repeat analyses of the GC samples from *trans*-2-butene reaction in the FTIR reactor shown in Table 3 typically exhibit little change with storage time in the transfer flask. This stability likely occurs because the concentration of the Cl_2 in these runs was low initially (∼75 mTorr) and significant amounts of Cl_2 had also been consumed during the reaction prior to sampling, thereby reducing the dark reaction rate further. The yields measured by GC analysis of the FTIR samples presented in Table 3 agree well with the FTIR analyses where comparisons are possible. The yields of the *cis*- and *trans*-1-chloro-2-butene from the FTIR reactor as measured by GC show that the ratio of trans to cis isomer varies over the range ∼7.5 to 9. Fortuitously, this ratio is similar to the ratio of the trans to cis isomers in the commercial 1-chloro-2-butene sample (ratio ∼6) used to obtain the FTIR calibration spectrum of this compound. Therefore, measurement of 1-chloro-2-butene using the FTIR instrument will provide a good estimate of the sum of the 1-chloro-2-butene isomers when studying the reaction of *trans*-2-butene, and the sum of the two isomers from FTIR measurements is presented in Table 3.

Also included in Table 3 are product yields determined by irradiation of mixtures in the GC reactor (runs A and B at 900 and 50 Torr total pressure, respectively). Comparison of the high-pressure data from the two reactors at the same initial reactant partial pressures (A, C, and D) shows that the yields from both reactors agree to within the stated experimental error. Total carbon balances are not included for the GC data because of the interferences caused by dark reaction particularly in the case of the *meso*-2,3-dichlorobutane isomer as discussed above,

TABLE 5: Product Yields Observed Following UV Irradiation of Cl_2/2-Butene/N_2/O_2 Mixtures

		2-C_4H_8[a] mTorr	Cl_2 mTorr	*P* (N_2)	*P* (O_2) Torr	$[C_4H_8]/[C_4H_8]_0$	*trans*-2-butene %[b]	CH_2O %[b]	CH_3CHO %[b]	CH_3COCl %[b]
						Trans				
A	FTIR	198[3]	210	0	700	0.8−0.4		4.6(0.7)	21(2)	8.7(1)
B	FTIR	223[6]	220	674	26	0.9−0.3		11(3)	40(6)	14(1.2)
C	FTIR[c]			100	600			4	16	9
D	FTIR[c]			675	25			10	32	15
						Cis				
E	FTIR	217[3]	219	553	147	0.9−0.5	≤2	10(1.5)	36(6)	8(1)
F	FTIR	235[3]	226	650	50	0.9−0.5	≤2	11(1.5)	38(4)	14(2)
G	FTIR	216[4]	226	690	10	0.9−0.4	≤2	10.5(1)	36(4)	16(1)
H	FTIR	237[3]	222	44	11	0.9−0.5	14(2)	9(1.5)	31(3)	11.5(1)
I	FTIR	245[3]	225	0	10	0.8−0.5	27(2)	6(0.7)	25(3)	8.7(0.8)

[a] Partial pressure of 2-butene in mixture [number of data points taken under the stated conditions shown in brackets]. [b] Mole percent product (per mole of 2-butene consumed) − estimated error in parentheses. [c] Data from Figure 10 of ref 3.

which can lead to large errors for this species. The agreement between the GC and FTIR experiments at 50 Torr (runs B and F in Table 3) is also reasonable, although at this pressure, the FTIR experiment showed somewhat elevated acetyl chloride and a reduced carbon balance, indicative of a significant elevation in the initial O_2 concentration.

Table 3 also shows the yield of the chlorine-atom-catalyzed isomerization product, *cis*-2-butene, determined by each analysis method. The yield of this product is sufficiently low for pressures near 1 bar that the FTIR sensitivity is not large enough to measure it within the complicated mix of spectra. However, GC measurements of reactions in the GC reactor and in samples taken from the FTIR reactor provide measurements of the yields of this product even at 700 Torr.

Table 4 presents data identical to those in Table 3 but for the reaction of *cis*-2-butene with Cl. Again, the product yields have been corrected for secondary consumption. Because the yield of the isomerization product (*trans*-2-butene) is much larger (particularly at low pressure) than the *cis*-2-butene isomerization product in Table 3, an additional correction was made. This correction removed the portion of the yield of the other products that arises from secondary consumption of the *trans*-2-butene to obtain a true product yield for the reactant *cis*-2-butene and was typically less than 15% of the uncorrected product yield. Data set A from the GC reactor and data set C from the FTIR reactor were obtained at essentially identical initial reactant partial pressures. The FTIR data set showed a low yield of acetyl chloride, indicating that the effect of oxygen contamination is not large. The GC and FTIR data agree to within the stated error limits in the case of *meso*-2,3-dichlorobutane and 3-chloro-1-butene. The DL-2,3-dichlorobutane yield in data set A does agree with the FTIR results to within the maximum error limits, but the GC measurement of this compound suffers from interference from dark reaction as described above and has a relatively large estimated error. The only product yield that differs significantly in the two reactors is the *trans*-2-butene isomerization product whose yield for $P \geq 700$ Torr is larger in the FTIR reactor as was also seen in Table 3. The estimated effect of dark reaction on the samples withdrawn from the FTIR reactor for GC analysis is generally larger than was estimated in Table 3. This is because most of the data sets in Table 4 were obtained at higher *cis*-2-butene partial pressure to improve the signal-to-noise ratio in the FTIR experiments, requiring a higher initial Cl_2 concentration.

Overall, the data in both reactors are consistent with the exception of the butene isomerization products at high total pressure. The general agreement between the results obtained from the two different experimental systems suggests that the products are formed by homogeneous reactions in both reactors. Also presented in Tables 3 and 4 are data from the liquid-phase experiments, which show product trends similar to the current gas-phase experiments.

3.4. Products Observed Following UV Irradiation of Cl_2/2-Butene Mixtures in N_2/O_2 Diluent. Table 5 presents the percentage molar yields of three major products (formaldehyde, acetaldehyde, and acetyl chloride) formed during the reactions of *trans*- or *cis*-2-butene with Cl atoms at several oxygen partial pressures in the FTIR reactor. The total pressure was varied over the range 10−700 Torr in the *cis*-2-butene experiments. The concentrations of formaldehyde, acetaldehyde, and acetyl chloride in the chamber increased linearly with the consumption of 2-butene, showing that these are primary products in this reaction.

The *trans*-2-butene data in Table 5 from the current experiments (runs A and B) were obtained at 700 Torr total pressure and O_2 partial pressures of 700 and 26 Torr, respectively. These data can be compared to product yields measured by Orlando et al. (Figure 10 of ref 3) at 700 Torr total pressure and O_2 partial pressures of 600 and 25 Torr, which are labeled runs C and D in Table 5. These authors determined that CH_3CHO, CH_2O, CH_3COCl, and $CH_3C(O)CH(Cl)CH_3$ have the largest molar yields and that the yields vary as a function of O_2 partial pressure. $CH_3C(O)CH(Cl)CH_3$ (3-chloro-2-butanone) was also a major product in the current experiments. This species is not included in Table 5 because its spectral features are very broad and are overlapped significantly by unidentified residual spectra. Therefore, an accurate measurement of its yield was not possible. The yields from the current experiments are in reasonable agreement with those of Orlando et al. at the same O_2 partial pressure (compare run A to run C, and run B to run D). The largest discrepancy occurs in the acetaldehyde yield where the data of ref 3 are approximately 20% lower than our results. A portion of this discrepancy may arise because our data have been corrected for secondary consumption by Cl while Orlando et al. did not state that they made such corrections. Removing this correction would decrease our yields by 10−15%, resulting in agreement to within the estimated experimental error. We conclude that the results of our product measurements in the presence of O_2 are indistinguishable from those reported by Orlando et al. No gas-phase product data are available for comparison to our data in N_2.

4. Discussion of Product Formation Mechanisms during UV Irradiation

4.1. Reactions in N_2 − Addition to the Double Bond. The only products observed upon UV irradiation of Cl_2/2-butene/

N_2 mixtures are 2,3-dichlorobutane (meso and DL), 1-chloro-2-butene (cis and trans), 3-chloro-1-butene, and the isomerized 2-butene. The 2,3-dichlorobutanes are formed by the addition of a chlorine atom to the double bond in 2-butene followed by reaction of the resultant 3-chloro-2-butyl radical with molecular chlorine:

$$\mathrm{Cl} + \mathrm{CH_3CH{=}CHCH_3} \rightarrow \mathrm{CH_3CH(\bullet)CH(Cl)CH_3} \quad (6)$$

$$\mathrm{CH_3CH(\bullet)CH(Cl)CH_3} + \mathrm{Cl_2} \rightarrow \mathrm{CH_3CH(Cl)CH(Cl)CH_3} + \mathrm{Cl} \quad (7)$$

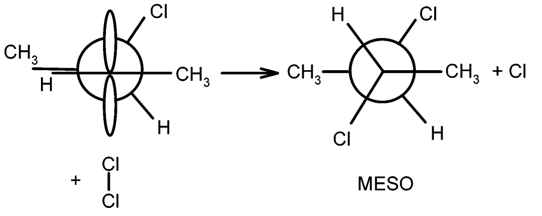
Based on the data in Tables 3 (data sets C, D, H, and I) and 4 (C, E, F, and G), the yields of the meso (~45−50%) and DL (~17−20%) stereoisomers at 700 Torr are identical to within experimental error for *cis*- and *trans*-2-butene and independent of reactant partial pressure. This indicates that the 3-chloro-2-butyl radical [$\mathrm{CH_3CH(\bullet)CH(Cl)CH_3}$] formed from each butene isomer via reaction 6 is a long-lived, collisionally stabilized radical whose distribution of stereoconfigurations is identical whether approached from either the *cis*- or the *trans*-2-butene reactant.

A recent publication by Neumann and Zipse[13] has examined the lowest energy and transition states of the 3-chloro-2-butyl radical using ab initio calculations at three levels of theory. Calculations at what the authors state to be the most reliable theory levels [G3(MP2)B3 or BHLYP/aug-cc-pVTZ] have identified two low-energy configurations for this radical separated by two transition states. The lowest energy configuration is one in which the methyl groups are located trans with respect to one another. A second stable configuration, which lies 0.85−1.15 kcal/mol above the trans configuration (depending upon the level of theory chosen), also exists in which the methyl groups are cis with respect to one another. These two configurations are connected by two transition states formed by rotation around the central C−C bond. The transition states are located 2.1−3.6 kcal/mol above the stable trans radical configuration (again depending upon the transition state and the level of theory). The low-energy cis and trans radicals are calculated to have the four carbon atoms in a nearly planar configuration with the Cl atom nearly perpendicular and the half-filled p-orbital on the sp^2 hybridized radical carbon atom perpendicular to that plane.

The theoretical calculations of Neumann and Zipse can provide a framework for understanding the observed ratios of the meso and DL stereoisomers of 2,3-dichlorobutane in these experiments. Although the rate constant for reaction 7 has not been measured, its value can be estimated to be $\sim 10^{-11}$ cm^3 molecule^{-1} s^{-1} based on the rate constant of the reaction of Cl_2 with the *sec*-butyl radical.[14] This estimated rate constant results in a lifetime of $\sim 10^{-5}$ s for the 3-chloro-2-butyl radical in the presence of 0.075−0.25 Torr of Cl_2. The rate constant for internal rotation of this alkyl radical can be estimated as $k_{\mathrm{rot}} \approx 10^{11.2}\ \mathrm{e}^{(-3300\mathrm{cal}/RT)}\ \mathrm{s}^{-1}$ using as an approximation the measurement by Benson et al.[4] of the internal rotation rate constant of the 3-iodo-2-butyl radical. This rate constant predicts a half-life for internal rotation of $\sim 10^{-9}$ s.

Because the lifetime of the 3-chloro-2-butyl radical is $\sim 10^4$ internal rotation half-lives, the cis and trans geometric configurations should be essentially thermally equilibrated in the lifetime of the radical. Based on the theoretical estimation of the energy difference between these two ground-state configurations (0.85−1.15 kcal/mol), a Boltzmann distribution would predict that the ratio of the populations in each of the radical configurations would be in the range trans/cis = 4 to 7. The observed ratio meso/DL is ~2.5−3. This suggests that the trans configuration of the 3-chloro-2-butyl radical is the likely source of the meso stereoisomer, which has the larger yield, and the cis configuration is the source of the DL stereoisomer. Because of the long life of the radical relative to its internal rotation rate, there should be no difference in the meso/DL ratio formed from the *cis*- and *trans*-2-butene isomers as is observed.

These arguments can be used to deduce a plausible orientation of the Cl_2 relative to the chlorobutyl radical during reaction 7. The stereoconfiguration of the trans radical during this reaction is shown in eq A to provide a better understanding of the mechanism. Equation A presents the stereochemistry of Cl_2 adding to the trans configuration of the 3-chloro-2-butyl radical (reaction 7) from below the plane of the 4 carbon atoms and, therefore, opposite to the position of the bonded Cl atom, which is shown above the plane. This addition process results in the formation of the 2,3-dichlorobutane stereoisomer shown on the right side of the reaction equation. The 2,3-dichlorobutane conformation shown in (A) has the Cl atoms anti to one another and the methyl groups anti to one another, characteristic of one orientation of the meso stereoisomer as discussed in section 3.1. If the Cl_2 were added from above the plane, next to the bonded Cl atom, this would form a 2,3-dichlorobutane in which the Cl atoms were nearly syn to one another and the methyl groups were anti to one another, characteristic of the DL stereoisomer contrary to the experimental data. Using a similar argument, addition of Cl_2 from below the plane to the cis form of the 3-chloro-2-butyl radical will result in formation of a 2,3-dichlorobutane in which the methyl groups are syn and Cl atoms are anti, which is one configuration of DL-2,3-dichlorobutane.

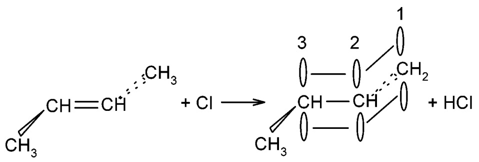


(A)

In summary, the yields of *meso*- and DL-2,3-dichlorobutane in N_2 can be semiquantitatively explained on the basis of the ab initio determination of the energy difference between the two low-energy stereo-orientations of the 3-chloro-2-butyl radical coupled with the requirement that the Cl_2 molecule approaches the radical from the side opposite to the location of the bonded chlorine atom in that radical. If the Cl_2 approached from the same side as the Cl atom in the 3-chloro-2-butyl radical, a meso/DL ratio opposite to that measured would be seen with the DL stereoisomer dominant.

4.2. Reaction in N_2 − Abstraction from a Methyl Group.

Abstraction of a hydrogen atom from a methyl group of 2-butene by Cl will form HCl and a methyl allyl radical, which has a bent C−C−C carbon chain analogous to that of the allyl radical. The data in Tables 3 and 4 show that the HCl yield equals the sum of the 1-chloro-2-butene and 3-chloro-1-butene yields to within experimental error. Equation B shows the stereochemistry of this process for *trans*-2-butene as the reactant. The methyl allyl radical subsequently reacts with Cl_2 at either the 1 or the 3 carbon position. Reaction at the 1 carbon position will form 1-chloro-2-butene, while reaction at the 3 carbon will form 3-chloro-1-butene. These two species are major products in the reaction as shown in Tables 3 and 4.



(B)

The data in Table 3 show that when the reactant is *trans*-2-butene, the 1-chloro-2-butene product is formed primarily (80−90%) but not exclusively in the trans configuration as illustrated in eq B. When the reactant is *cis*-2-butene (Table 4), the predominant (but, again, not sole) isomer formed is *cis*-1-chloro-2-butene. This indicates that the barrier for breaking the delocalized, allylic bond to allow rotation about the C−C bond between carbons 2 and 3 must be sufficiently large that reaction with Cl_2 is fast enough to trap the methyl allyl radical largely in its original configuration at ambient temperature. However, the 1-chloro-2-butene is not formed solely in this configuration. Isomerized 1-chloro-2-butene is formed for both *cis*- and *trans*-2-butene reactants, although at a lower yield. Korth et al.[15] determined the rate constant for internal rotation within the allyl radical to be $k_{\mathrm{rot}} = 10^{13.5}\ \mathrm{e}^{-15700\mathrm{cal}/RT}\ \mathrm{s}^{-1}$. No data are available for internal rotation in the methyl allyl radical, to our knowledge, but it is reasonable to assume that the activation energy and *A* factor will be similar. Using the allyl rate expression (k_{rot}), the rate constant for internal rotation at 298 K is 97 s^{-1} and the half-life for internal rotation will be ~0.01 s. This process is in competition with reaction 8, which determines the half-life of the methyl allyl radical. The rate constant for reaction 8 has been measured at 298 K ($k_8 = 1.1 \times 10^{-14}$ cm^3 $\mathrm{molecule}^{-1}$ s^{-1}),[16] and this rate constant yields a half-life for the methyl allyl radical of ~0.01−0.04 s, for Cl_2 partial pressures of 0.25 and 0.075 Torr, respectively. Based on these rate expressions, the internal rotation rate is competitive with the radical lifetime, and some isomerized 1-chloro-2-butene may be formed by this process. The isomerized methylallyl radical can also be formed via an addition elimination reaction as discussed in the following section.

$$CH_3{-}CH{-}CH{-}CH_2\ \text{(methyl allyl)} + Cl_2 \rightarrow \text{products} \quad (8)$$

4.3. Reactions via a Chemically Activated 3-Chloro-2-butyl Radical. Isomerization of *cis*-2-butene to *trans*-2-butene and trans to cis is observed both in the presence and in the absence of O_2 (Tables 3−5). The yields of *cis*-2-butene observed following reaction of *trans*-2-butene with Cl atoms are listed in Table 3. The yield of *cis*-2-butene is too small to be measured accurately by FTIR at 700 and at 50 Torr of N_2, but by taking samples from the FTIR reactor for GC analysis, the yield was determined to be 2.5% and 5% at 700 and at 50 Torr total pressure, respectively. Isomerization was also observed during experiments in the GC reactor. At 50 Torr total pressure, the yield in the GC reactor (run B in Table 3) agreed to within experimental uncertainty with the sample taken from the FTIR reactor for GC analysis (run F in Table 3). However, at 700 Torr total pressure, there is a discrepancy that appears to be outside of the estimated error limits (compare data sets A and D). At 10 Torr total pressure, the yield was large enough (12%) to be measured by the FTIR spectrometer. Therefore, based on these data, the isomerization yield depends on pressure. It also depends on the reactor used but only at the highest pressure (e.g., lowest yield). Where possible, the following discussion will be based on FTIR data only, because these data are affected less by uncertainty caused by possible hetereogeneous processes such as the dark reaction discussed above and more data have been obtained using the FTIR apparatus. However, it is important to note that generally consistent trends were obtained from the GC and FTIR reactors.

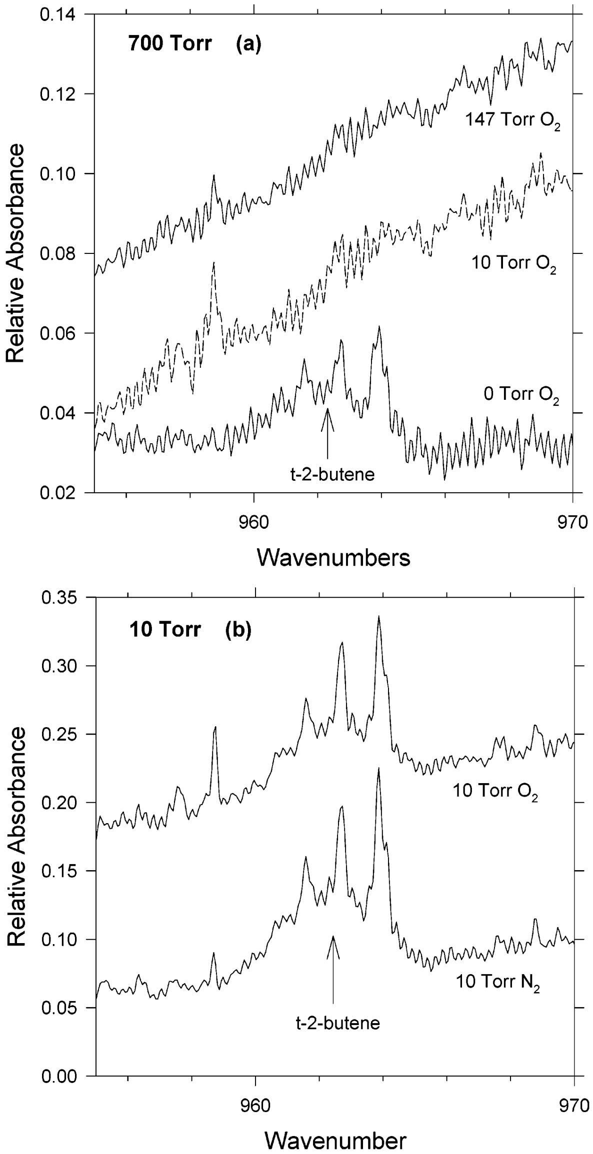


Figure 5. FTIR absorption spectra of the *trans*-2-butene product from the reaction Cl + *cis*-2-butene at two total pressures (10 and 700 Torr) and varying O_2 partial pressures.

To explore this isomerization process in more detail, experiments were performed on the reaction of *cis*-2-butene with Cl at three total pressures in the FTIR reactor. *cis*-2-Butene has several advantages in studying this phenomenon. First, as shown in Table 4, the yield of the *trans*-2-butene at 10 Torr total pressure (35%) from cis reactant is approximately 3 times larger than the yield of *cis*-2-butene (12%) when *trans*-2-butene is the reactant (see Table 3), increasing the signal-to-noise ratio (S/N). In addition, the absorption band used for the quantification of *trans*-2-butene is stronger than that of the *cis*-2-butene band, which increases the S/N more. A series of experiments with *cis*-2-butene as the reactant was performed in the presence and in the absence of O_2 at three total pressures (10, 50, and 700 Torr) and at three O_2 partial pressures (10, 50, and 147 Torr) at 700 Torr.

Figure 5a and b presents sample spectra obtained during experiments quantifying the *trans*-2-butene product yields. Figure 5a shows the IR absorption in the region 955−970 cm^{-1} at 700 Torr total pressure with O_2 partial pressures of 0, 10, and 147 Torr. The percentage *cis*-2-butene consumed in each

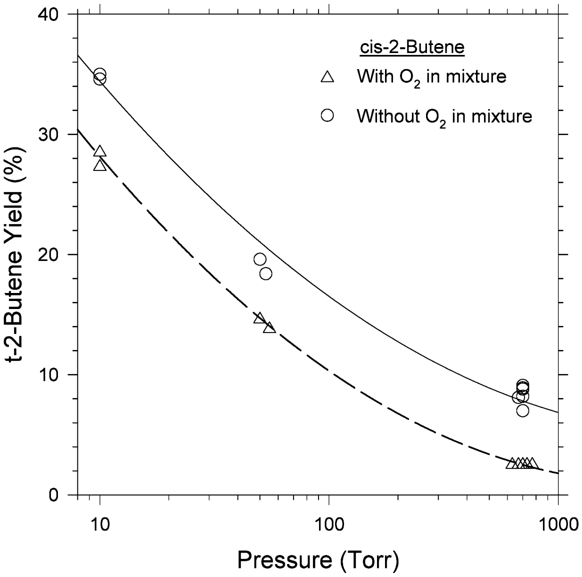


Figure 6. Yield (%) of *trans*-2-butene from the reaction (Cl + *cis*-2-butene) as a function of total pressure. The data represented by ○ were obtained in N_2 diluent. △ represent data obtained in the presence of O_2 at partial pressures from 10 to 700 Torr with N_2 added to obtain the total pressure desired. At 10 Torr total pressure, both O_2 data points were obtained at 10 Torr of O_2. At 50 Torr total pressure, the O_2 data points were obtained at 10 and 50 Torr of O_2. Data at 700 Torr in the presence of 10−700 Torr of O_2 represent upper limits (see text).

of the three data sets was similar (50 ± 5%). The spectrum at 700 Torr of N_2 ($O_2 = 0$ Torr) shows that there is an absorption feature in this spectral range, which is comprised of a broad band with three sharp features characteristic of *trans*-2-butene, located between 959 and 966 cm^{-1}. Adding 10 Torr of O_2 suppresses this absorption at 700 Torr to the extent that, while it is possible that there may still be some of this species present, its absorption is very near to the noise level. Furthermore, the suppression of the isomerization product is essentially complete at 10 Torr of O_2. To within experimental error, there is no change in the absorbance in this wavenumber range as the O_2 partial pressure is increased from 10 to 147 Torr.

Figure 5b presents the absorbance at 10 Torr total pressure of either N_2 or O_2. The *cis*-2-butene consumption for each data set is 48 ± 2%. The absorbance is much stronger at 10 Torr (N_2) than at 700 Torr, because of the larger yield of *trans*-2-butene at low pressure, and the percentage change in the absorbance caused by addition of O_2 is much smaller than is observed at 700 Torr. An O_2 (and total) pressure of 10 Torr reduces the absorption intensity modestly at this pressure relative to 10 Torr of N_2. It does not suppress it almost entirely as is the case at 10 Torr of O_2 with 690 Torr of N_2 in Figure 5a.

Figure 6 presents the measured yields of *trans*-2-butene from the isomerization reaction as a function of total pressure both in the presence and in the absence of O_2. As described above, the data points at 700 Torr in the presence of O_2 are actually upper limits to the true yields because the FTIR signal is near the noise level. GC analyses of products from the FTIR reactor, however, do verify that *trans*-2-butene is present with a yield of ∼2−3% for mixtures containing 10−147 Torr of O_2 at 700 Torr total pressure. The data in Figure 6 indicate that addition of O_2 reduces the *trans*-2-butene yield by ∼6−7% of the *cis*-2-butene consumed at all three pressures tested. Based on this observation, it appears that there are two sources for formation of *trans*-2-butene. One (equal to the difference in yield between the data without O_2 and that with O_2) is independent of total pressure to within the data scatter with a yield of 6−7%. The second source, represented by the yield curve in the presence of O_2, depends strongly on the total pressure ($\sim P^{-0.6}$), but, based on the data at 50 and 700 Torr, is essentially independent of O_2 partial pressure over the range 10−700 Torr. This pressure-dependent source of *trans*-2-butene likely results from rapid internal rotation about the central C−C bond of the chemically activated 3-chloro-2-butyl radical that is the initial result of the addition of Cl to *cis*-2-butene and does not live long enough to react with O_2.

$$cis\text{-}2\text{-}C_4H_8 + Cl \leftrightarrow 2\text{-}C_4H_8Cl^* \qquad (6a)$$

$$2\text{-}C_4H_8Cl^* \rightarrow trans\text{-}2\text{-}C_4H_8 + Cl \qquad (6b)$$

$$2\text{-}C_4H_8Cl^* + M \rightarrow C_4H_8Cl \qquad (6c)$$

As discussed in section 4.1, the half-life for internal rotation of a stabilized 3-chloro-2-butyl radical is estimated to be $\sim 10^{-9}$ s. At 1 atm and 298 K, the collision frequency in N_2 is $\sim 5 \times 10^9$ s^{-1}, resulting in a time between collisions of $\sim 2 \times 10^{-10}$ s. At 10 Torr total pressure, the time between collisions will be $\sim 10^{-8}$ s. Therefore, the collision frequency within the total pressure range of 10−700 Torr is of the proper magnitude to influence the lifetime of the activated radical within a rotational lifetime, assuming that its half-life for internal rotation is at least as fast as that estimated for the stabilized radical. This supports the suggestion that, at 700 Torr, the chemically activated intermediate is likely to be quenched quickly enough that little internal rotation occurs prior to the collisional stabilization of the radical. In that case, little isomerization will occur at high pressure, but more can occur at lower pressure because the lifetime of the chemically activated radical will be longer, explaining the observed pressure dependence.

We have no mechanistic explanation for the 6−7% yield of *trans*-2-butene that is suppressed by the presence of 10 Torr or more O_2 and has no measurable pressure effect. Such a source could be explained by internal rotation of a stabilized 3-chloro-2-butyl radical if this radical could then lose its Cl atom and return to 2-butene. No measurement of the C−Cl bond strength in this radical is available, to our knowledge. However, it is reasonable to assume that it would be similar to that of the 2-chloro-1-ethyl radical whose bond strength has been calculated to be ∼17 kcal/mol.[17] A bond strength of this magnitude would not allow loss of Cl from the 3-chloro-2-butyl radical to be competitive with its reaction with Cl_2 at ambient temperature.

The chemically activated 3-chloro-2-butyl radical could also contribute to the formation of *cis-/trans*-1-chloro-2-butene and 3-chloro-1-butene, which were stated to be abstraction products in section 4.2. In a study of the reaction of Cl with propylene,[11] a reaction channel was observed, which appeared to be a pressure-dependent abstraction process. This was ascribed to reaction of a chemically activated chloropropyl adduct, which decomposed in a pressure-dependent reaction to the allyl radical plus a molecule of HCl. A similar channel could occur via decomposition of the chemically activated 3-chloro-2-butyl radical formed in reaction 6a:

$$CH_3CH(Cl)CHCH_3^* \rightarrow CH_2CHCHCH_3 \text{ (methylallyl)} + HCl \qquad (6d)$$

The combination of reactions 6a and 6d produces a stabilized methylallyl radical, which can form *cis-/trans*-1-chloro-2-butene and 3-chloro-1-butene as described in the discussion of the abstraction reaction.

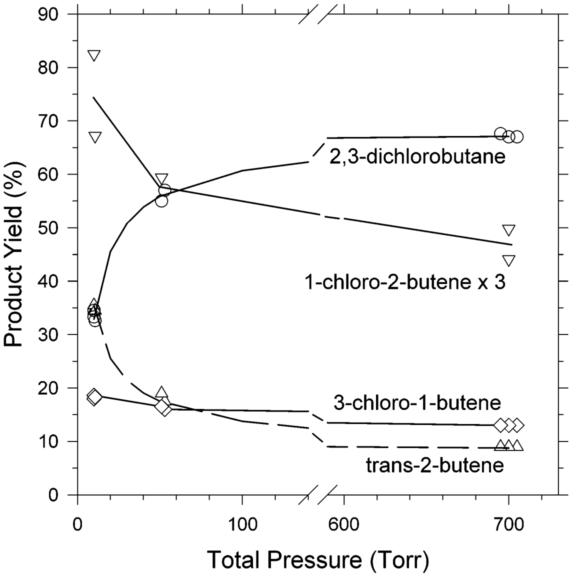


Figure 7. Yields of the products of the reaction of Cl with *cis*-2-butene as a function of total pressure of N_2. Points are from data sets E−L in Table 4.

The pressure dependence of the product yields can provide insight into the impact of the chemically activated 3-chloro-2-butyl radical on the reaction chemistry. The observation that the overall rate constant of reaction 2 is essentially pressure independent might suggest that the product yields would also be independent of pressure because the reaction seems to be near to its high-pressure limit. However, the product yields do change very significantly with pressure as is shown in Figure 7. A unique aspect of this reaction is that, because different stereoisomers are present in the products, information can be deduced concerning the effects on the product yields of both stable intermediate radicals and the chemically activated 3-chloro-2-butyl radical. In the majority of addition reactions, the activated complex decomposes back to the initial reactant, and little direct information can be obtained from the products about this decomposition process except that it is pressure dependent. However, in the *cis*-2-butene case, the activated complex generated from reaction 6a can decompose to either the initial reactant or its isomeric species, *trans*-2-butene. Thus, to a first approximation, the product yield from the addition reaction is the sum of the *trans*-2-butene and the 2,3-dichlorobutane yields. This approximation neglects any effect of reaction 6d, which will be examined in subsequent paragraphs.

At 10 Torr total pressure, *trans*-2-butene and the sum of the *meso*- and DL-2,3-dichlorobutane stereoisomers contribute approximately ∼35% and 33%, respectively, to the total product yield as shown in Figure 7. As the pressure increases to 700 Torr, the yield of the 2,3-dichlorobutane isomers increases to 68%, while the *trans*-2-butene decreases to ∼8% based on the data in Figure 7, which is also tabulated in Table 4 (see data sets E−L). This shows that, as the pressure increases, the yield of the *trans*-2-butene product from the chemically activated complex decreases sharply while the 2,3-dichlorobutane product derived from the stabilized 3-chloro-2-butyl radical becomes dominant. Much of the change in yields of these products has occurred by a total pressure of 50 Torr. The *trans*-2-butene yield in Figure 7 represents the sum of the O_2-dependent and -independent yields. As discussed above, there is an O_2-dependent yield (∼6−7%), which is independent of total pressure. Thus, the pressure-dependent portion of the *trans*-2-butene yield in Figure 7, which results from the chemically activated chlorobutyl radical, is obtained by subtracting ∼6.5% from the yields plotted in Figure 7 (and also shown in Figure 6). After this correction was made, the pressure-dependent yield displays an even larger pressure dependence, decreasing from 29% at 10 Torr to approximately 2% at 700 Torr.

The 3-chloro-1-butene product yield formed from the methylallyl radical also decreases with increasing total pressure from 18% at 10 Torr to 13% at 700 Torr. This decrease of a factor of 1.4 is much smaller than the factor of 14 decrease in the yield of the pressure-dependent component of the *trans*-2-butene yield. This indicates that approximately $^3/_4$ of the 3-chloro-1-butene yield actually arises from an intermediate methylallyl radical unrelated to the chemically activated 3-chloro-2-butyl radical. This is consistent with the formation of this portion of the 3-chloro-1-butene via a methylallyl radical generated by direct hydrogen abstraction from a methyl group in *cis*-2-butene as discussed in section 4.2. Methylallyl radical generated by abstraction will be pressure independent. Based on a comment by a referee, it is also conceivable that HCl elimination could occur from the stabilized 3-chloro-2-butyl radical to yield a pressure-independent methylallyl radical. The heat of formation of the 3-chloro-2-butyl radical is not available, to our knowledge, and this path cannot be ruled out on thermodynamic grounds.

The yield of 1-chloro-2-butene also decreases with increasing total pressure. However, the magnitude of this decrease is subject to more uncertainty (as shown by the data scatter) than that of 3-chloro-1-butene. The reason for this increased uncertainty is the fact that 1-chloro-2-butene must be determined from GC analysis of samples removed from the FTIR reactor rather than being measured directly in the infrared, adding additional uncertainty to the measurement. The repeatability of species yields measured by FTIR spectroscopy is excellent as a function of pressure as shown both in Figure 7 and in Table 4. The repeatability of the GC measurements is not as good. However, the ratio of the *cis*- and *trans*-1-chloro-2-butene isomers is determined well by GC because any error introduced by sampling will affect both isomers equally. Table 4 shows that decreasing the total pressure in the FTIR experiments increases the yield of *trans*-1-chloro-2-butene relative to that of the cis isomer. This is consistent with the hypothesis that lower pressures cause generation of more 1-chloro-2-butene via the chemically activated 3-chloro-2-butyl radical. As discussed above, the lifetime of this activated radical increases with decreasing pressure. Therefore, more of the isomerized methylallyl radical will be formed at low pressure, leading to an increase in the yield of the isomerized 1-chloro-2-butene product.

In summary, the data suggest that the chemically activated 3-chloro-2-butyl radical plays a relatively small role in determining the product yields at 700 Torr. At 10 Torr, however, it plays a very critical role in the distribution of the products from reaction 2b. While reaction 2a was not studied extensively as a function of pressure, data sets H and I in Table 3 are consistent with the above statements, although the uncertainties are substantially larger. One important observation regarding the reaction of Cl with *trans*-2-butene is that the yield of *cis*-2-butene at 10 Torr from reaction 2a is much smaller (12%) versus that (35%) from reaction 2b. This observation may result from the fact that isomerization of *trans*- to *cis*-2-butene is endothermic by approximately 750 cal/mol while isomerization of *cis*- to *trans*-2-butene is exothermic.

5. Conclusions

We present a large body of data concerning the kinetics and products of the reactions of Cl atoms with *cis*- and *trans*-2-

butene [reaction 2] in N_2 and in N_2/O_2 diluent over a wide range of total pressure (10−900 Torr). Consistent results were obtained using the two different experimental systems (GC and FTIR reactors). The data enable us to draw the following conclusions:

(1) A heterogeneous dark reaction occurs between molecular chlorine and the 2-butenes. This reaction forms only *meso*-2,3-dichlorobutane from *trans*-2-butene and only DL-2,3-dichlorobutane from *cis*-2-butene. A small yield of 3-chloro-1-butene is also formed during the dark reaction.

(2) The rate constant for reaction 2 determined using the relative rate technique is observed to be essentially pressure independent from 10 to 700 Torr. The rate constants for the *cis*- and *trans*-2-butene isomers are indistinguishable within the experimental uncertainties and agree with previous determinations at ambient pressure.

(3) In N_2 diluent, the products formed are *meso*- and DL-2,3-dichlorobutane, 3-chloro-1-butene, *cis*- and *trans*-1-chloro-2-butene, and the isomerized 2-butene (i.e., *trans*-2-butene from *cis*-2-butene reactant). The meso/DL ratio is identical for *cis*- and *trans*-2-butene reactants. Both reactants form similar yields of 3-chloro-1-butene. In contrast, *cis*-1-chloro-2-butene is the principal 1-chloro-2-butene species formed from *cis*-2-butene, while primarily *trans*-1-chloro-2-butene is formed from *trans*-2-butene. The ratio of the yields of *cis*- and *trans*-1-chloro-2-butene is pressure dependent. The yield of the isomerized 2-butene is also pressure dependent. These data can be used to obtain insight into the reaction mechanism. Three primary reaction channels are proposed.

(4) The first channel is the normal addition reaction to the double bond to produce a stable 3-chloro-2-butyl radical. Based on ab initio calculations in the literature, this radical has two orientational configurations represented by energy minima separated by ~1 kcal/mol. We believe that the lower energy minimum generates the *meso*-2,3-dichlorobutane via reaction with Cl_2, while the higher energy minimum yields the DL-2,3-dichlorobutane isomer. The ratios of the yields of these isomers (meso/DL $\approx$ 2.5−3) from *cis*- and *trans*-2-butene reactants are indistinguishable and are consistent with that expected from a Boltzmann distribution of the populations of these two butyl radical minima, which are randomized during the lifetime of the chlorobutyl radical.

(5) The second channel forms the pressure-dependent isomerized 2-butene product. This channel proceeds through a chemically activated 3-chloro-2-butyl radical that results from the initial addition of a Cl atom to a 2-butene molecule, producing a yield that depends strongly on pressure. The isomerization occurs because of rotation about the central C−C bond in the chemically activated radical before dissociation back to either *cis*- or *trans*-2-butene.

(6) The third channel forms *cis*- and *trans*-1-chloro-2-butene and 3-chloro-1-butene, whose yields have both pressure-dependent and pressure-independent components. We believe that these products are both formed from a methylallyl radical reaction with Cl_2. The methylallyl radical can be formed either by: (a) direct hydrogen abstraction from a methyl group of 2-butene, which is pressure independent and maintains the stereo-orientation of the original 2-butene; or (b) intramolecular HCl elimination from the chemically activated 3-chloro-2-butyl radical. The latter process is pressure dependent and allows rotation about the central C−C bond as discussed in conclusion (5). This results in a pressure-dependent component to the 1-chloro-2-butene and 3-chloro-1-butene yields. It also produces a pressure dependence to the cis/trans ratio of 1-chloro-2-butene.

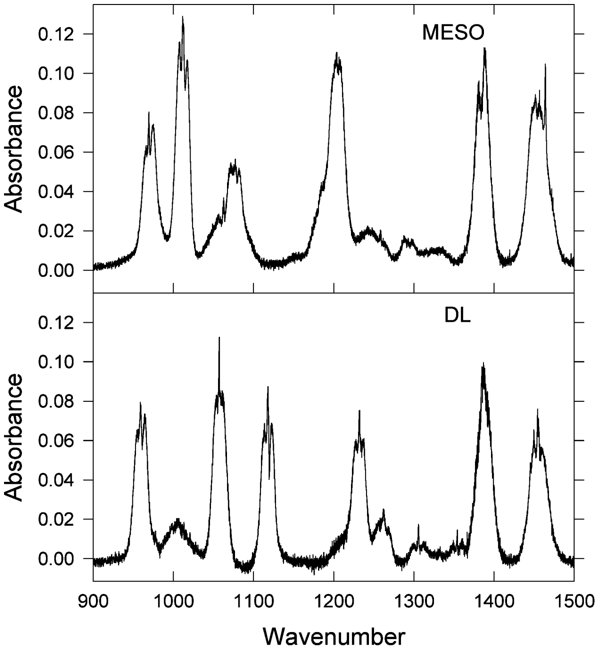


Figure 8. FTIR spectra of meso (19.5 mTorr) and DL (15.8 mTorr) 2,3-dichlorobutane in 700 Torr of N_2.

Appendix A. Infrared Spectra of *meso*- and DL-2,3-Dichlorobutane

Figure 8 presents the FTIR spectra of *meso*- and DL-2,3-dichlorobutane. These spectra were obtained by deconvolution of the IR spectra from mixtures of 2,3-dichlorobutane purchased from two suppliers. As discussed in sections 2.1 and 2.2, these two mixtures had significantly different meso/DL ratios based on GC analyses, making the deconvolution possible.

Appendix B. Rate Constants for Reaction of Product Species with Cl

Limited experiments were performed to measure the rate constants of the reactions of Cl with 3-chloro-1-butene (k_{31}), 1-chloro-2-butene (k_{12}), and 2,3-dichlorobutane (k_{23}) at 900 Torr in N_2 using the relative rate technique with GC analysis. The value of k_{31} was measured three times relative to propane (1.43×10^{-10}). The measured rate constant is $k_{31} = (2.1 \pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Using propane as the reference in three experiments, $k_{12} = (2.2 \pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The value of k_{23} was determined relative to both ethane (5.9×10^{-11} cm^3 molecule^{-1} s^{-1})[18] and ethyl chloride (8.7×10^{-12})[19] in two and four experiments, respectively. Both reference compounds yielded a value $k_{23} = (1.1 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. These rate constants are used to correct the product species yields for secondary consumption by Cl.

Appendix C. Effect of Contaminant O_2 on Product Yields

As presented in section 3.3, the effect of O_2 contamination is much greater on the products arising from the methylallyl radical reaction with Cl_2 (3-chloro-1-butene and 1-chloro-2-butene) than on the 2,3-dichlorobutane product from reaction of the 3-chloro-2-butyl radical with Cl_2. To our knowledge, no measurements are available that compare the rates of reaction of Cl_2 to that with O_2 for either the 3-chloro-2-butyl radical or the methylallyl radical. Such knowledge is critical to rationalizing the observed effect. However, data are available for the allyl radical and for the 2-butyl radical. At 298 K, the rate constant[16] for the reaction (allyl + Cl_2) is 1×10^{-14} cm^3

molecule^{-1} s^{-1}, while the rate constant[20] for the reaction (allyl + O_2) is 6×10^{-13} cm^3 molecule^{-1} s^{-1}. Thus, the allyl radical reacts ~60 times faster with O_2 than with Cl_2. Conversely, the rate constant for the reaction of the 2-butyl radical with Cl_2 has been measured[21] relative to that with O_2, yielding the ratio, k(2-butyl + Cl_2)/k(2-butyl + O_2) = 2.8 ± 0.1. Assuming that the methylallyl and 3-chloro-2-butyl radicals follow similar trends, the products formed from the methylallyl radical will be much more sensitive to O_2 contamination than will the 2,3-dichlorobutane product from the 3-chloro-2-butyl radical, as the experimental data indicate.

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