J. Am. Chem. Soc. **1989**, *111*, 2845–2849

Our future efforts will be concentrated to reveal the circumstances in which local acidification due to fluctuations may take place. Our ultimate aim is to find and interpret more systems exhibiting the theoretically predicted[23] and recently experimentally verified[22,24,25] fluctuation-induced reactions.

Acknowledgment. The helpful discussions with Prof. I. R. Epstein and the technical assistance of Ágnes Bálint is highly appreciated. This work was supported by the Hungarian Academy of Sciences (Grant No. 391/1988).

Registry No. $S_2O_3^{2-}$, 14383-50-7; $S_4O_6^{2-}$, 15536-54-6; $S_2O_4^{2-}$, 14844-07-6; SO_3^{2-}, 14265-45-3; $S_2O_6^{2-}$, 14781-81-8; $N_2H_5^+$, 18500-32-8; BrO_3^-, 15541-45-4; IO_3^-, 15454-31-6; ClO_3^-, 14866-68-3; ClO_2^-, 14998-27-7; $S_2O_8^{2-}$, 15092-81-6.

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Molecular Structures of Unstable Dichloroketene and Its Precursor, Trichloroacetyl Chloride, from Electron Diffraction[1]

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Abstract: The molecular structure of dichloroketene, Cl_2CCO, has been determined at room temperature by electron diffraction. Cl_2CCO was produced from trichloroacetyl chloride, Cl_3CCOCl, with zinc at 420 °C during the diffraction experiment. Analysis of data of the reaction product, containing about 30% of trichloroacetyl chloride, has yielded the following geometrical parameters (r_a) of Cl_2CCO, with estimated total errors: C=C 1.299 ± 0.005, O=C 1.160 ± 0.003, Cl—C 1.726 ± 0.004 Å, and ∠Cl—C=C 120.4 ± 0.2°. The structure of Cl_3CCOCl has been determined separately from diffraction data of its vapor. For a model in which the O=C bond eclipses a Cl—CCl_2 bond, the bond lengths (r_a) and angles are C—C 1.540 ± 0.008, O=C 1.191 ± 0.004, Cl—CO 1.727 ± 0.017, Cl—CCl_2 1.774 ± 0.006 Å, ∠C—C=O 121.4 ± 0.7°, ∠C—CO—Cl 113.8 ± 0.7°, ∠(Cl—C—CO)$_{mean}$ 109.7 ± 0.4°.

I. Introduction

The geometric and electronic structures of highly reactive ketene derivatives have motivated several recent studies on monohalogeno- and dihalogenoketenes by microwave,[3,4] infrared[5–7] and photoelectron spectroscopy,[8,9] and ab initio calculations.[4] Geometrical parameters were obtained for ClHCCO from microwave spectra,[3] and for FHCCO from ab initio calculations.[4] Dichloroketene, Cl_2CCO, was shown to have a very small dipole moment, and its microwave spectrum could not be observed.[6]

In the present work we have undertaken the structure determination of dichloroketene. This is a continuation of our studies of unstable species that have so far included halogenated carbene analogues AX_2 (A = Si, Ge; X = Cl, Br[10]) and the allyl radical.[11] Cl_2CCO was generated from trichloroacetyl chloride, Cl_3CCOCl, in a flow system during the diffraction experiment, and the reaction product was a mixture of the two substances. Although the structures of other halogen-substituted acetyl halides have been published,[12–15] no structure determination of Cl_3CCOCl is known to us. Thus, the study of Cl_2CCO had to be accompanied by the structure analysis of Cl_3CCOCl.

II. Experimental Section

Trichloroacetyl chloride was obtained from Cl_3CCOOH by its reaction with $SOCl_2$ and purified by distillation and repeated vacuum freezing.[7] Dichloroketene was produced by the high-temperature reaction of vapors of Cl_3CCOCl with metallic zinc:[8]

$$Cl_3CCOCl + Zn \xrightarrow{\Delta} Cl_2CCO + ZnCl_2$$

Figure 1 shows the schematic arrangement of the reactor nozzle system. The quartz tube (4) of 7-mm inner diameter tapers in a nozzle (11) of 0.4-mm outlet diameter. This end of the tube is covered with a graphite layer and is contacted to an earthed metal block (10) to prevent charging by the electron beam. The heated zone (7a), which is 7 cm long, lies outside the diffraction chamber, at about 30-cm distance from the nozzle. The construction of the connection and the sealing between the tube and the wall of the chamber ensured a stable position of the nozzle regardless of temperature changes in the reaction zone. Our previous experience[7] and investigations of vapor composition by a quadrupole mass spectrom-

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[1] This paper is dedicated to the memory of Andrei K. Maltsev (1933–1986), one of the pioneers of structural research of unstable species.

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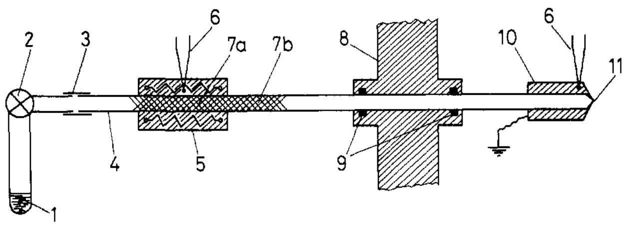

Figure 1. Schematic cross section of the reactor nozzle system: (1) liquid sample, (2) Teflon valve, (3) connecting Teflon tube, (4) quartz tube, (5) heater, (6) thermocouple, (7) zinc filling, (7a) hot zone, (7b) cold zone, (8) wall of the diffraction chamber and adjusting device, (9) rubber "O" rings, (10) metal block, (11) nozzle.

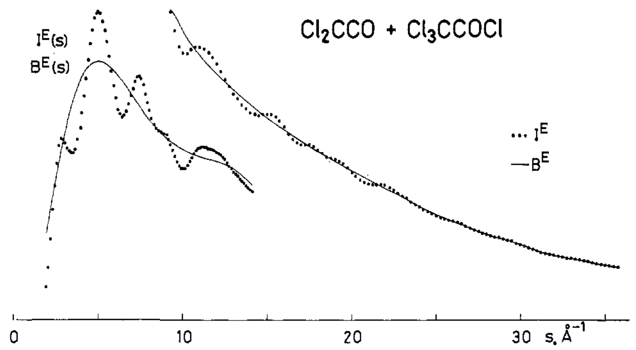

Figure 2. Total experimental intensities (I^E) and backgrounds (B^E) of the mixture of Cl_2CCO and Cl_3CCOCl.

eter[16] helped us to find favorable conditions for both the production of Cl_2CCO and the electron diffraction experiment. First, the diffraction pattern of Cl_3CCOCl was taken using the reactor nozzle system at room temperature. Then, the reactor temperature was raised and kept just below the melting point of Zn, and the diffraction pattern of the reaction mixture was photographed. Considering possible temperature differences within the reactor, the maximum temperature could be 415 to 420 °C. An unheated section (7b) of the zinc chops served to trap the $ZnCl_2$ and Zn vapors. The nozzle itself was close to room temperature; 25 to 29 °C was measured in the enveloping metal block (10) during the exposures in both experiments. Since at the time of the experiments we were too optimistic about the possibilities of analyzing data from the reaction product, we took only one photograph of the diffraction pattern of Cl_3CCOCl at each camera distance. Eventually it proved necessary to elucidate the structure of Cl_3CCOCl as well, and having only one plate for each camera range, of course, resulted in a relatively high data noise in the subsequent analysis. However, this approach was judged to be more advantageous from the point of view of the analysis of Cl_2CCO than to run additional independent experiments for Cl_3CCOCl.

The diffraction experiments were performed in Budapest in a modified[17] EG-100A unit, using 50- and 19-cm camera distances, 60-kV accelerating voltage, and Kodak electron image plates. The electron wavelength was calibrated with polycrystalline TlCl.[18] An empirical blackness correction was applied to transform optical densities of the photographic plates into electron intensities. Details of data reduction, procedures of structure analysis, and error estimation are described elsewhere.[19] Refinement of structural parameters was based on reduced molecular intensities in ranges

$$1.875 \le s \le 14.125 \text{ and } 9.250 \le s \le 35.750 \text{ Å}^{-1}$$

for the mixture, and

$$2.125 \le s \le 14.125 \text{ and } 9.750 \le s \le 34.000 \text{ Å}^{-1}$$

for Cl_3CCOCl, with data intervals of 0.125 and 0.250 $Å^{-1}$ in the two ranges, respectively, and unit weights for all data points. A modified version of a least-squares program[20] was used. Coherent[21] and incoherent[22] scattering factors were interpolated from tabulated values.

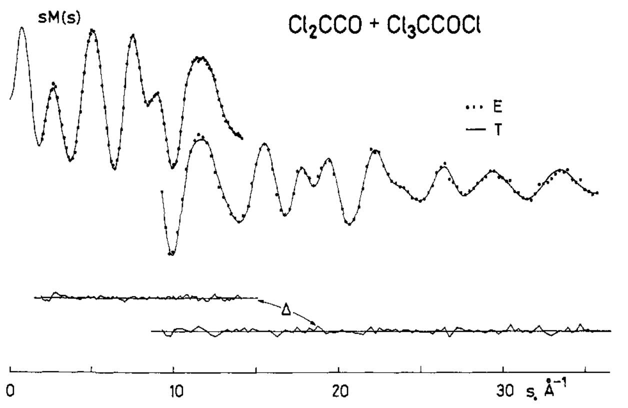

Figure 3. Experimental (E) and theoretical (T) molecular intensities (*sM*) and their differences ($\Delta = E - T$) for the mixture of Cl_2CCO (72.7%, Table I) and Cl_3CCOCl (27.3%, *r* and *l* from Table II).

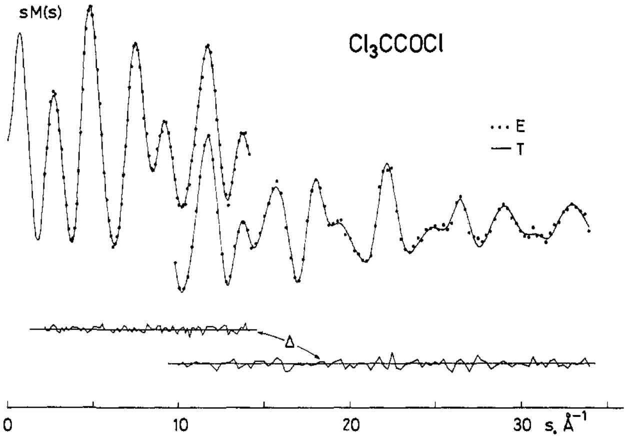

Figure 4. Molecular intensities and the difference curves of Cl_3CCOCl (Table II).

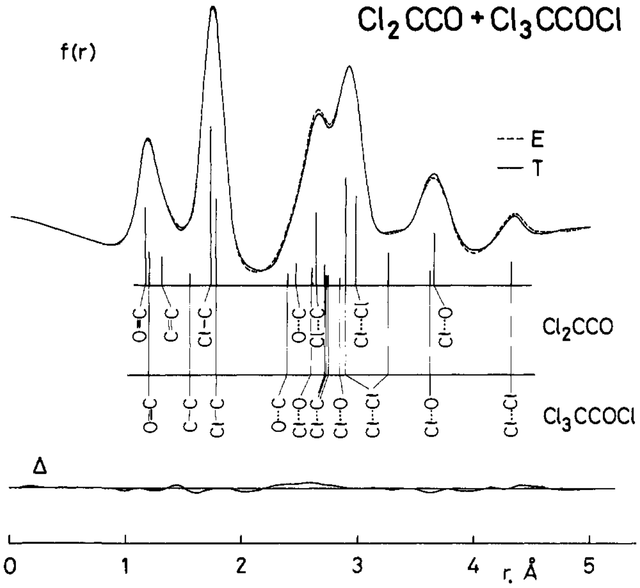

Figure 5. Experimental (E) and theoretical (T) radial distributions and the difference curve ($\Delta = E - T$) of the mixture. Damping constant $a = 0.002$ $Å^2$. Contributions from Cl_2CCO (72.7%) and Cl_3CCOCl (27.3%) are indicated separately. Cf. Tables I and II.

Total experimental intensities and background lines for the mixture are shown in Figure 2, molecular intensities for the mixture and Cl_3CCOCl in Figures 3 and 4. The total intensity values are deposited as supplementary material.

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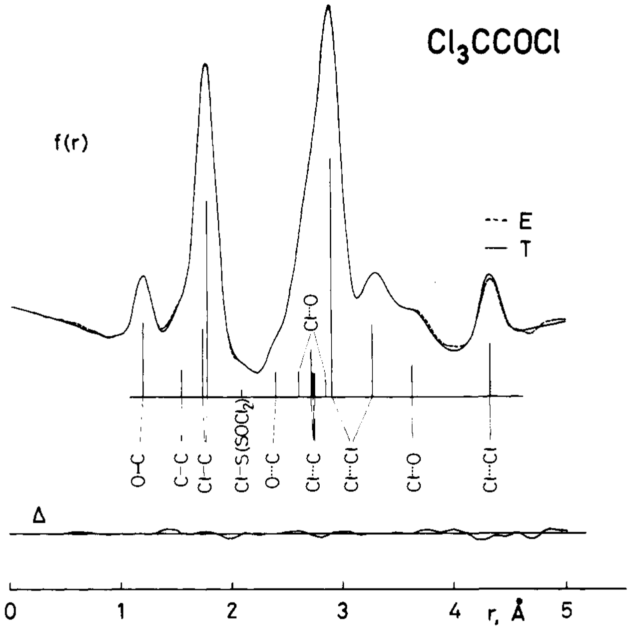

Figure 6. Radial distributions and the difference curve of Cl_3CCOCl. Damping constant $a = 0.002$ Å^2. Contributions from Cl_3CCOCl (97.2%) and from the Cl—S bond of $SOCl_2$ (2.8%) are shown; cf. Table II.

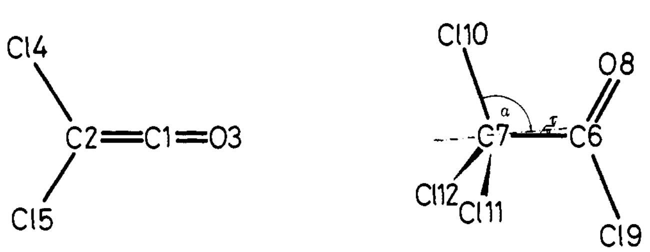

Figure 7. Numbering of atoms and definition of angles.

III. Structure Analysis

An inspection of the radial distribution curves (Figures 5 and 6) reveals the presence of trichloroacetyl chloride in the reaction product in addition to dichloroketene. It is also seen that all features of the radial distribution of the mixture contain contributions from both components, except for the peak at 4.3 Å, which originates from Cl_3CCOCl only. This leads to serious correlations between the parameters of the two molecules.

The geometry of molecular models of Cl_3CCOCl was defined by distance parameters C—C, O=C, $(Cl—C)_{mean}$, and Δ(Cl—C), i.e., the difference of the bond lengths Cl—CCl_2 and Cl—CO, and by angles C—C=O, C—CO—Cl, α, and τ (Figure 7). The distinct peak at 4.3 Å assigned to the Cl···Cl anti interaction led to the assumption that the Cl_3C group eclipses the O=C bond, and possesses C_{3v} symmetry with a tilt in the Cl—C—C=O plane; α is the obtuse angle of the Cl—CCl_2 bonds to the symmetry axis; the tilt angle τ is positive if the in-plane Cl—C—CO bond angle is larger than α. Initial values of the mean vibrational amplitudes (l) were transferred from related molecules.[12,13] Amplitudes were grouped in the refinements according to regions of the radial distribution, with fixed differences within the groups. One of the angles or Δ(Cl—C) was fixed in some refinements. Fixed parameters and initial values of refined parameters were systematically varied in reasonable ranges in order to explore possible multiple solutions.

Diffraction data of the vapors of Cl_3CCOCl yielded relatively well-determined parameters for this molecule (see Table II), in spite of some correlation between angles and C—C and Cl—C bond lengths and amplitudes. The tilt angle is negligible and thus α is practically equal to the mean Cl—C—CO bond angle.

The molecular geometry of Cl_2CCO was characterized by bond lengths C=C, O=C, Cl—C and bond angle Cl—C=C. The assumption of planarity of the molecule is justified by the planarity of ketene,[23] fluoroketene,[4] and chloroketene.[3] There was no indication of experimentally detectable shrinkages on the radial distributions; hence, in view of the difficulties imposed by parameter correlation, no perpendicular vibration corrections or shrinkage parameters were applied, and the C=C=O chain in Cl_2CCO was assumed to be linear. The tilt parameter of Cl_3C-COCl has certainly taken care of at least part of the shrinkage

Table I. Structural Parameters of Dichloroketene[a]

parameter[b]	r_a, Å $\angle_a$, deg	σ_{LS}	σ_t	l(ED), Å	σ_{LS}	σ_t	l(SP), Å
	Independent Parameters						
C=C	1.299	3	5	0.065	5	8	0.041
O=C	1.160	2	3	0.035	3	4	0.035
Cl—C	1.726	1	4	0.049	1	3	0.047
∠Cl—C=C	120.4	1	2				
	Dependent Distances						
O3···C2	2.459	3	7	0.063	7	10	0.045
Cl4···C1	2.634	2	6	0.071	2	4	0.064
Cl4···Cl5	2.976	2	8	0.073	2	6	0.052
Cl4···O3	3.650	2	8	0.097	3	5	0.086
$p(Cl_2CCO)$	0.727	7	10				
$p(Cl_3CCOCl)$	0.273	7	10				
k_{50}	1.803	17					
k_{19}	1.909	30					
R_{50}	0.051						
R_{19}	0.108						
R	0.071						

[a] Parameters of Cl_3CCOCl have been fixed at the values given in Table II. l(ED)'s are from electron diffraction; l(SP)'s have been calculated from spectroscopic data. σ_{LS}, the standard deviations from the least-squares procedure, and σ_t, the estimated total errors (see text), are in units of the last digit of the parameter. [b] See Figure 7 for the numbering of atoms. p's are the mole fractions, k's are the factors included in sM^T to make it match sM^E, and $R^2 = \Sigma(sM^E - sM^T)^2/\Sigma(sM^E)^2$, and subscripts 50 and 19 refer to the two camera ranges.

Table II. Structural Parameters of Trichloroacetyl Chloride[a]

parameter[b]	r_a, Å $\angle_a$, deg	σ_{LS}	σ_t	l(ED), Å	σ_{LS}	σ_t	
	Independent Parameters						
C—C	1.540	6	8	0.050	3	4	II
O=C	1.191	2	4	0.031	4	5	I
$(Cl—C)_{mean}$	1.762	1	4				
Δ(Cl—C)	0.047	15	21				
∠C—C=O	121.4	5	7				
∠C—CO—Cl	113.8	5	7				
α	109.7	3	4				
τ	0.4	4	6				
	Dependent Distances						
Cl—CO	1.727	12	17	0.049	3	4	II
Cl—CCl_2	1.774	3	6	0.049	3	4	II
O8···C7	2.387	7	11	0.047	8	10	III
Cl9···O8	2.598	18	26	0.082	9	12	IV
Cl11···C6	2.709	4	8	0.090	9	12	IV
Cl10···C6	2.719	11	16	0.090	9	12	IV
Cl9···C7	2.739	8	12	0.090	9	12	IV
Cl10···O8	2.844	20	28	0.163	1	4	V
Cl10···Cl11	2.894	1	6	0.070	1	2	V
Cl9···Cl11	3.262	4	9	0.139	4	6	VI
Cl11···O8	3.620	5	11	0.140	7	10	VII
Cl9···Cl10	4.317	3	10	0.070	3	5	VIII
$p(Cl_3CCOCl)$	0.972	8	11				
$p(SOCl_2)$	0.028	8	11				
k_{50}	1.468	20					
k_{19}	1.420	30					
R_{50}	0.046						
R_{19}	0.126						
R	0.069						

[a] For notation, see footnotes to Table I. Roman numerals indicate the coupling scheme of amplitudes. [b] See text and Figure 7 for the definition of parameters and numbering of atoms.

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Table III. Geometrical Parameters of Ketene Derivatives and Related Molecules

molecule		C=C, Å	O=C, Å	X—C, Å	∠X—C=C, deg	X	ref
H_2CCO	r_z	1.3165 (15)	1.1614 (14)	1.0800	119.01	H	23
CH_3HCCO	r_s	1.306	1.171	1.518	122.6	CH_3	35
$(CH_3)_2CCO$	r_0	1.300 (12)	1.171[a]	1.514 (6)	120.6 (3)	CH_3	36
$(Me_3Si)_2CCO$	r_a	1.318 (13)	1.16[a]	1.886 (4)[b]	116	Me_3Si	37
$(Me_3Ge)_2CCO$	r_a	1.274 (15)	1.16[a]	1.946 (5)[b]	116.2 (7)	Me_3Ge	38
FHCCO[c]		1.326	1.168	1.354	120.0	F	4
ClHCCO[d]		1.316[a]	1.161[a]	1.726	119.8	Cl	3
Cl_2CCO	r_a	1.299 (5)	1.160 (3)	1.726 (4)	120.4 (2)	Cl	*e*
Cl_2CO	r_g, $\angle_z$		1.184 (3)	1.744 (1)	124.1[f]	Cl	39
Cl_2CCH_2	r_g, $\angle_\alpha$	1.334 (4)		1.728 (2)	122.9	Cl	40
Cl_2CCCl_2	r_g	1.354 (3)		1.718 (3)	122.2	Cl	30

[a] Assumed parameter. [b] Mean Si—C and Ge—C bond distance, respectively. [c] Empirically corrected ab initio results. [d] From microwave spectroscopy, one of the possible structures. [e] Present work. [f] Angle Cl—C=O.

Table IV. Geometrical Parameters of Chloro-Substituted Acetyl Chlorides

molecule		C—C, Å	O=C, Å	Cl—CO, Å	Cl—CXY,[a] Å	$(Cl—C)_{mean}$, Å	∠C—C=O, deg	∠C—CO—Cl, deg	ref
H_3CCOCl	r_g, $\angle_\alpha$	1.508 (5)	1.187 (3)	1.798 (3)		1.798 (3)	127.5 (9)	112.2 (9)	42
ClH_2CCOCl[b]	r_a, $\angle_\alpha$	1.521 (9)	1.182 (4)	1.772 (16)	1.782 (18)	1.777 (3)	126.9 (9)	110.0 (7)	12
$Cl_2HCCOCl$[b]	r_g, $\angle_\alpha$	1.535 (8)	1.189 (3)	1.752 (9)	1.771 (4)	1.765 (3)	123.3 (13)	113.9 (59)	13
Cl_3CCOCl	r_a	1.540 (8)	1.191 (4)	1.727 (17)	1.774 (6)	1.762 (4)	121.4 (7)	113.8 (7)	*c*

[a] X, Y = Cl, H. [b] Results for room temperature. Bond distances and bond angles were assumed to be equal in the two coexistent conformers. [c] Present work.

of the longest Cl···Cl distance if there was any at all. Initial l values were calculated from a force field which was based on those of ketene[24] and 1,1-dichloroethene[25] and which was fitted[26] to the five available experimental frequencies of Cl_2CCO.[7]

Parameters of Cl_2CCO and Cl_3CCOCl and a composition variable were fitted to the experimental molecular intensities of the mixture, using different refinement schemes. With fixed parameters of Cl_3CCOCl, taken from Table II, small systematic deviations from the experimental curves could not be eliminated (Figures 3 and 5). If, however, all of the parameters of Cl_3CCOCl were also allowed to vary, no stable minimum was achieved in the least-squares refinement, and Δ(Cl—C) and the angles in Cl_3CCOCl became ill-defined. Then some of these parameters were fixed to different values. Similar bond distances in Cl_2CCO and Cl_3CCOCl, viz. O=C and Cl—C, were refined either independently or with their differences between Cl_2CCO and Cl_3CCOCl fixed. Bond lengths C=C in Cl_2CCO and C—C in Cl_3CCOCl had strong correlation with O=C and Cl—C, respectively, and with the corresponding amplitudes; l(C=C), if treated separately, tended to be unrealistically high. Some conditions of the refinement, unfortunately, did influence the resulting parameters of Cl_2CCO and, to a larger extent, those of Cl_3CCOCl. Striking variations occurred in the Cl4···Cl5 and Cl10···Cl11 distances as a consequence of ambiguity in resolving their similar contributions to the peak at 2.9 Å of the radial distribution curve (Figure 5). The difference in the parameters of Cl_3CCOCl as obtained from the two experiments cannot be explained by possible changes in the experimental conditions: the nozzle temperature was practically the same when the diffraction pattern of the starting material and that of the reaction product were photographed.

The presence of possible further components in the mixture was also tested. It has been found[7,8,27,28] that Cl_2CCO decomposes, although at higher temperatures than used in our experiments, to give carbon monoxide and tetrachloroethene as a dimerization product of dichlorocarbene. A contribution from CO + $1/2C_2Cl_4$ to the theoretical molecular intensities was therefore calculated with fixed geometrical[29,30] and vibrational[31a,32] data taken from the literature. Refinement of parameters of Cl_2CCO and Cl_3CCOCl and the composition variables unambiguously showed the absence, within error limits, of these decomposition products in our experiment. Since mass spectra of Cl_3CCOCl indicated the presence of small amounts of $SOCl_2$ from the synthesis, we suspected that the faint feature at 2.1 Å on the experimental radial distribution of Cl_3CCOCl (Figure 6) could be due to the Cl—S bond in $SOCl_2$. Therefore, we included this component with fixed parameters[33] in the refinement. It was found that the sample of Cl_3CCOCl could contain up to 3% of $SOCl_2$, but its introduction did not affect the parameters of Cl_3CCOCl. On the other hand, no $SOCl_2$ could be detected by a similar approach in the reaction product, and its possible presence was thus ignored in further analyses.

IV. Results and Discussion

Final parameters of dichloroketene (Table I) have been taken from the refinement with fixed parameters of Cl_3CCOCl, which formed about 30% of the mixture. These parameters of trichloroacetyl chloride (Table II) were the ones obtained from the diffraction data of its vapors in the separate experiment. Estimated total errors[19] (σ_t) include standard deviations from the least-squares procedure (σ_{LS}), estimated systematic (scale) errors of 0.2% for distances and 2% for l values, and, in the case of Cl_2CCO, a possible effect of the bias caused by constraining the parameters of Cl_3CCOCl.[34]

The bond lengths of Cl_2CCO are similar to corresponding parameters of related molecules (Table III). No feature of the geometry of Cl_2CCO suggests instability of this molecule. The fact that halogenoketenes survive relatively long times for transportation in various experiments also indicates their relative stability. The mean amplitudes l(ED) for C=C and O3···C2

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(Table I) seem to be too large; calculated amplitudes for the corresponding distances in C_3O_2 are 0.038 and 0.043 Å, respectively.[41] If they bear any reality and are not merely results of parameter correlation, the large values might indicate some propensity for dissociation. Cl_2CCO decomposes at lower temperatures[28] than ketene itself. l(SP) of Cl_2CCO should be treated with caution, too, because of the small number of available experimental frequencies.[7] Our l(SP) for Cl4···Cl5, e.g., is too small compared to the calculated value 0.0691 Å in Cl_2CO.[31b]

The parameters of Cl_3CCOCl fit well the trends observed[13] in the series of chlorosubstituted acetyl chlorides (Table IV): the C—C bond lengthens and the Cl—CO bond and the carbon–chlorine bonds on the average shorten as the number of chlorine substituents increases from acetyl chloride to its trichloro derivative. The bond angle C—C=O decreases in the same series.

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Registry No. Cl_3CCOCl, 76-02-8; Cl_2CCO, 4591-28-0.

Supplementary Material Available: Tables of total experimental electron diffraction intensities (2 pages). Ordering information is given on any current masthead page.

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Piezochromism: Pressure-Induced Rearrangements of Thermochromic and Related Cu(II) Complexes Containing Asymmetrically Substituted Ethylenediamine

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Abstract: The effects of high pressure on the thermochromic and related complexes $[CuL_2]X_2$ [L = *N,N*-diethylethylenediamine (dieten), X = BF_4^-, ClO_4^-, Cl^-; L = *N,N*-dimethylethylenediamine (dimeen), X = BF_4^-; L = ethylenediamine (en), X = BF_4^-] are described. Electronic and infrared spectroscopies indicate an increase in the interaction between anion and molecular CuN_4 plane of all complexes with increasing pressure. For both the electronic and infrared spectra, the similarity between the high-pressure spectra of the dieten complexes and the low-pressure spectra of the en and dimeen complexes indicates that the former transform to a geometry similar to that of the latter with pressure. A color change is associated with the transformation. The short pressure range over which the rearrangement occurs in the crystal indicates that it is a highly cooperative process. Studies of some of the complexes in polymeric environments [sodium polystyrenesulfonate and/or poly(2-vinylpyridine)] show that the rearrangement occurs at lower pressure and is much less cooperative in the polymers.

Many of the complexes $[Cu(dieten)_2]X_2$, where X is an anion and dieten is *N,N*-diethylethylenediamine, exhibit interesting behavior with temperature and have been the subject of a number of physical investigations.[3-8] When X is BF_4^-, ClO_4^-, or NO_3^- the complex exhibits a dramatic color change from a red low-temperature form to a blue form at a well-defined higher temperature.[4,9] This thermochromic behavior was originally attributed by Lever et al.[4] to a temperature-dependent axial interaction between the anion and the CuN_4 plane and later was demonstrated to be due to a weakening of the in-plane ligand field strength as a result of the onset of dynamic disorder of the chelate rings as the temperature is raised.[7,8]

Ferraro et al.[5] studied the effect of pressure (0–48 kbar) on the infrared and electronic band maximum of these complexes and concluded that no significant change in axial interaction occurs with increasing pressure. These workers argue that the primary effect of pressure is to contract the in-plane copper–nitrogen distances, thereby minimizing the axial interaction causing no color change.

In this paper we investigate the effect of pressure to 150–200 kbar on the electronic and infrared spectra of the complexes $[CuL_2]X_2$ [L = *N,N*-diethylethylenediamine (dieten), X = BF_4^-, ClO_4^-, and Cl^-; L = *N,N*-dimethylethylenediamine (dimeen), X = BF_4^-; L = ethylenediamine (en), X = BF_4^-). Gaussian resolution of the electronic spectra are reported. In addition to the polycrystalline studies, the electronic spectra of some of the complexes were studied as dopants in a sodium polystyrenesulfonate (L = dieten, X = BF_4^-, ClO_4^-) or poly(2-vinylpyridine) (L = dieten, X = Cl^-, BF_4^-) environment.

Experimental Procedure

Sample Preparation. The ligands en, dimeen, and dieten were obtained from Aldrich and used without further treatment. The en complexes were prepared by the method of Procter,[10] while the dimeen and dieten

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