125. *The Infrared Absorption Spectra of Some Chloroformates and Carbonates. The Structure of "Di- and Tri-phosgene".*

By J. L. HALES, J. IDRIS JONES, and W. KYNASTON.

The infrared absorption spectra of some chloroformates and carbonates (both open chain and cyclic) have been determined with special reference to the C=O and C–O stretching vibrations. In particular, the effect of chlorine substitution in the α- and the β-position has been examined. The structures $CCl_3{\cdot}O{\cdot}CO{\cdot}Cl$ and $CCl_3{\cdot}O{\cdot}CO{\cdot}O{\cdot}CCl_3$ respectively, have been confirmed. The ease of dissociation of compounds containing the ${\cdot}CO_2{\cdot}CCl_3$ group into carbonyl chloride is discussed.

THE terms " di- and tri-phosgene " which are frequently applied to trichloromethyl chloroformate (I) and bistrichloromethyl carbonate (II), respectively, are misnomers since these compounds are not derived from carbonyl chloride; they are prepared by exhaustive chlorination of methyl formate (or chloroformate) and methyl carbonate, respectively.[1–5] However, in most reactions (I) and (II) behave as two and three molecules of carbonyl chloride respectively, into which they readily dissociate.[3, 6, 7] Thiocarbonyl chloride, on the other hand, dimerises photochemically and the dimer can be depolymerised. Originally thought to be the dithio-analogue of (I), this dimer has been shown to be 2 : 2 : 4 : 4-tetrachloro-1 : 3-dithia*cyclo*butane.[8] Similar cyclic structures have been postulated for the related silicon compound [9] and the corresponding siliconoxyhalides, and selenohalides [10, 11] An analogous structure (III) for " diphosgene " would be consistent with some properties, particularly, its tendency to dissociate into carbonyl chloride. Similarly, the chemical

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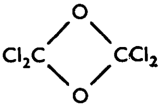
[1] Councler, *Ber.*, 1880, **13**, 1697.
[2] Hentschel, *J. prakt. Chem.*, 1887, **36**, 99, 209.
[3] Hood and Murdock, *J. Phys. Chem.*, 1919, **23**, 498.
[4] Kling, Florentin, Lassieur, and Schmitz, *Ann. Chim.*, 1920, **13**, 44.
[5] Grignard, Rivat, and Urbain, *ibid.*, pp. 228, 263.
[6] Nekrassow and Melnikow, *J. prakt. Chem.*, 1930, **126**, 81; **127**, 210.
[7] Melnikow, *ibid.*, **128**, 233.
[8] Hales, Jones, and Kynaston, preceding paper.
[9] Etienne, *Bull. Soc. chim. France*, 1953, 791.
[10] Schumb and Holloway, *J. Amer. Chem. Soc.*, 1941, **63**, 2753.
[11] Weiss and Weiss, *Angew. Chem.*, 1954, **66**, 714.

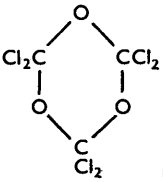
behaviour of " triphosgene " could be interpreted in terms of the perchlorinated 1 : 3 : 5-trioxan (IV). An early German patent [12] describes the addition of carbonyl chloride to chloral to give two products which were assumed to be 1 : 2 : 2 : 2-tetrachloroethyl chloroformate and bistetrachloroethyl carbonate, but they could be represented as cyclic compounds since chloral is known to form mixed polymers of the substituted trioxan type with a number of aldehydes.[13–15]

(I) $Cl\cdot CO_2\cdot CCl_3$

(II) $CO(O\cdot CCl_3)_2$



(III)



(IV)

The infrared absorption spectra of " diphosgene " and " triphosgene " and the two products from the carbonyl chloride–chloral reaction have been studied as part of a survey of those of chloroformates and carbonates, including products of the reaction of carbonyl chloride with epoxides.[16]

The infrared absorption spectrum of carbonyl chloride has been studied by Bailey and Hale [17] but spectroscopic data for chloroformates and carbonates are scanty. The Raman spectra of methyl, ethyl, propyl, and trichloromethyl chloroformates have been examined.[18, 19] Bailey and Hale [17] found a value of 1827 cm.$^{-1}$ for the C=O frequency in gaseous carbonyl chloride, which agrees with a later determination by Nielson, Burke, Woltz, and Jones.[20] In carbon tetrachloride solution we found the C=O frequency in carbonyl chloride at 1792 cm.$^{-1}$. Both " di- " and " tri-phosgene " exhibit strong absorption in the same region, at 1795 cm.$^{-1}$ and 1832 cm.$^{-1}$, respectively (Tables 1 and 2). This evidence and that for related compounds, which illustrate the influence of structural factors on the frequency of both C=O and C–O bands, confirm structures (I) and (II) for " di " and " tri-phosgene." Comparison of the spectrum of " triphosgene " with those of trioxan and paraldehyde, neither of which shows intense absorption in the 1800 cm.$^{-1}$ region, affords further support for structure (II). Similarly, strong carbonyl absorption at 1793 and 1794 cm.$^{-1}$, respectively, was found in the spectra of the two products from the carbonyl chloride–chloral condensation, thus ruling out dioxa*cyclo*butane and dioxan structures. It is noteworthy that 1 : 2 : 2 : 2-tetrachloroethyl alcohol is identical with the so-called chloral hydrochloride prepared by Vorländer and Siebert.[21]

The main bands in the ranges 1850—1700 cm.$^{-1}$ and 1300—950 cm.$^{-1}$ of the spectra of a series of chloroformates and carbonates are listed in Tables 1—3. Most of the compounds were examined as liquids and in solution but, with the exception of the cyclic carbonates, differences were small. However, band shifts between liquid and solution were greater in the cyclic carbonates and any comparisons between cyclic carbonates should therefore be made between corresponding states.

Much information is available concerning the vibrational frequency of the C=O bond and its dependence upon various structural factors.[22] Highly electronegative atoms tend

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[12] F. Bayer and Co., G.P. 121,223/1901.
[13] Pinner, *Ber.*, 1898, **31**, 1926.
[14] Helferich and Besler, *ibid.*, 1924, **57**, 1279.
[15] Hibbert, Gillespie, and Montonna, *J. Amer. Chem. Soc.*, 1928, **50**, 1953.
[16] Idris Jones, to be published.
[17] Bailey and Hale, *Phil. Mag.*, 1938, **25**, 98.
[18] Joglekar, *ibid.*, 1937, **24**, 405.
[19] Kohlrausch and Sabathy, *Monatsh.*, 1939, **72**, 303.
[20] Nielsen, Burke, Woltz, and Jones, *J. Chem. Phys.*, 1952, **20**, 596.
[21] Vorländer and Siebert, *Annalen*, 1905, **341**, 21.
[22] Hartwell, Richards, and Thompson, *J.*, 1948, 1436.

to increase the carbonyl frequency;[23] thus, in carbonyl chloride the frequency is 1827 cm.$^{-1}$ and in carbonyl fluoride 1928 cm.$^{-1}$, whereas in formaldehyde the corresponding vibration has a frequency of 1745 cm.$^{-1}$. Similarly, a high carbonyl frequency is observed in acid

TABLE 1. *Chloroformates*, CCl·CO·OX.

No.	X	State	$\nu_{C=O}$, cm.$^{-1}$.	ν_{C-O},[a] cm.$^{-1}$
1	Me	SN	1777	1202 m, *1149* s
		L	1776	1200 m, *1147* s
2	Et	S′N	1773	*1159* s, *1138* s, 1012 m
		L	1777	*1160* s, *1140* s, 1008 w
3	$CH_2·CH_2Cl$	SN	1775	*1143* s
4	$CHMe·CH_2Cl$	L	1779	*1170* s, 1132 s, 1030 m
5	CHMe·CHMeCl	L	1776	*1170* s, 1132 m, 1082 m, 1064 m
6	$CH(CH_2Cl)_2$	L	1776	*1155* s
7	2-Chloro*cyclo*hexyl	L	1771	*1168* s, 1117 m
8	$CHPh·CH_2Cl$	L	1770	*1146* s
9	$CHCl·CCl_3$	SN	1793	*1108* s, 997 m
10	CCl_3	SN	1806	*1056* s, 970 s, 913 s

[a] It is not suggested that all the bands listed are due to the C–O stretching vibration. The strongest band(s) is/are italicised.

SN = Solution (CCl_4); S′N = solution (CS_2); L = liquid; N, D, or F = solid in Nujol, KCl disc, or thin film, respectively.

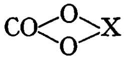
s = strong, m = medium, w = weak band.

Unlabelled bands are strong.

TABLE 2. *Carbonates*, XO·CO·OY.

No.	X	Y	State	$\nu_{C=O}$, cm.$^{-1}$	ν_{C-O},[a] cm.$^{-1}$
11	Me	Me	SN	1755	*1280* s, 974 m
			L	1748	*1280* s, 970 m
12	Et	Et	SN	1739	*1262* s, 1022 s
13	$CH_2·CH_2Cl$	$CH_2·CH_2Cl$	SN	1750	1306 m, 1272 s, *1246* s, 1006 m
14	$CHMe·CH_2Cl$	$CHMe·CH_2Cl$	L	1743	1277 s, *1256* s, 1202 m, 1135 m, 1034 m
15	CHMe·CHMeCl	CHMe·CHMeCl	L	1743	*1268* s, 1158 *w*, 1085 m, 1060 m
16	$CH(CH_2Cl)_2$	$CH(CH_2Cl)_2$	SN	1741	*1254* s, 1207 s, 1014 m
17	2-Chloro*cyclo*-hexyl	2-Chloro*cyclo*-hexyl	N(i)[b]	1743	*1257* s, 1009 m, 947 m
			N(ii)	1746	*1262* s, 1006 m, 948 m
18	$CHPh·CH_2Cl$	$CHPh·CH_2Cl$	N	1751	*1226* s
19	$CHCl·CCl_3$	$CHCl·CCl_3$	SN	1794	*1240* s, 1073 s, 992 s
20	CCl_3	CCl_3	SN	1832	*1178* s, 967 s, *945* vs
21	CCl_3	Et	L	1780	~*1235* s, ~1085 s, ~1000 s
22	Me	Ph	L	1755	*1262* s, 1215 s, 1064 m
23	Et	Ph	L	1757	*1252* s, 1209 s, 1060 m
24	Et	$C_6H_4·O·CO_2Et$	L	1756	*1234* s
25	Ph	Ph	S′N	1775	*1227* s, 1182 s, 1159 m

[b] (i) and (ii) refer to the two stereoisomeric modifications, m. p.s 65—66° and 111° (see Experimental section).

TABLE 3. *Cyclic carbonates*, 

$CO\langle{}^{O}_{O}\rangle X$

No.	X	State	$\nu_{C=O}$, cm.$^{-1}$	ν_{C-O},[a] cm.$^{-1}$
26	$·CH_2–CH_2·$	SN	1817, 1763 sh, w	*1138* s, *1077* s, 962 w
		S′N	1817, 1763 sh, w	*1138* s, *1077* s, 962 w
		L	1795, 1770 sh, m	*1163* s, *1073* s, 970 m
		F	1788, 1762 sh, m	1175 m, *1065* s, 971 m
27	$·CHMe–CH_2·$	SN	1809	*1171* s, *1115* s, 1084 w, *1058* s
		L	1792	*1182* s, 1119 m, 1076 sh, m, *1051* s
28	$·CHCl–CH_2·$	L	1828, 1797 sh, m	*1151* s, *1078* s, 1046 m, 965 s
29	·CHCl–CHCl·	L	1852, 1794 sh, m	*1115* s, *1087* s, 1026 s, 976 s
30	$·CH(CH_2Cl)–CH_2·$	L	1803	*1165* s, *1072* s, 1045 m
31	$·CHPh–CH_2·$	S′N	1816	*1152* s, *1067* s, 1052 sh, m
		D	1770	1182 sh, s, *1164* s, 1064 sh, s, *1051* s
		S′N	1832, ~1770 w	*1160* s, *1089* s
32	·CH=CH·	SN	1833, ~1770 w	*1160* s, *1089* s
		L	1830 s, 1801 sh, s	*1162* s, *1100* s, *1084* s
		F	1822 s, *1796* s	1170 m, 1157 m, *1105* s, 1075 s
33	$[\overset{|}{C}H–\overset{|}{C}H]_n$	N	1833	*1162* s, *1084* s

chlorides and, in the chloroformates, the same effect operates. In methyl and ethyl formates[24] the C=O band appears at 1723 cm.$^{-1}$ whereas in the corresponding chloroformates (Table 1) it is at 1775 cm.$^{-1}$. In compounds 1—8 (Table 1) the frequency of the carbonyl vibration is fairly constant, implying that neither the mass of group X nor the presence of a β-chloro-atom in the group X has any significant effect. However, substitution of chlorine atoms at the α-carbon atom in the group X produces a shift in the carbonyl band to higher frequencies, as seen in compounds 9 and 10. In the carbonate series (Table 2) this effect of α-chlorine substitution is again apparent (compounds 19—21). It is also known that esters containing the structure $CO_2C{:}C$ show slight enhancement of the carbonyl frequency regardless of whether the double bond is normal or part of an aromatic ring.[25] This effect shows up in diphenyl carbonate (Table 2) and in the cyclic vinylene carbonate (Table 3). In the cyclic carbonates the C=O group forms part of a five-membered ring and the influence of ring strain is evident. As with four- and five-membered ring ketones, lactones, and anhydrides the strain induces a shift of the carbonyl vibration to higher frequencies.[25] This strengthening of the C=O bond with ring strain has been discussed from a theoretical standpoint by Coulson and Moffitt.[26] Chlorine substitution on the α-carbon atom in the cyclic carbonates also produces a shift in the carbonyl frequency (compounds 28 and 29) whereas a β-chloro-atom, as before, has little effect (compound 30). Another interesting observation in the series of cyclic carbonates is the appearance in some, but not all, of two carbonyl bands close together which, in two cases examined, show differences between solution and liquid and solid states. Thus, ethylene carbonate in solution in carbon tetrachloride or carbon disulphide gives a strong carbonyl band at 1817 cm.$^{-1}$ with a weak shoulder at 1763 cm.$^{-1}$. In the liquid the main band is at 1795 cm.$^{-1}$ and the shoulder at 1770 cm.$^{-1}$. In the solid the band at 1788 cm.$^{-1}$ is again accompanied by a shoulder at 1762 cm.$^{-1}$ which appears more pronounced. The effect is far more definite in vinylene carbonate; dilute solutions in carbon disulphide and carbon tetrachloride show intense absorption at 1832 cm.$^{-1}$ with weak absorptions at 1802 and 1770 cm.$^{-1}$; in concentrated carbon tetrachloride solution the band at 1802 cm.$^{-1}$ is intensified. In the liquid the main band appears at 1830 cm.$^{-1}$ with a strong shoulder at 1801 cm.$^{-1}$ but in the solid the latter band, slightly shifted to 1796 cm.$^{-1}$, is somewhat stronger than the first band which now appears at 1822 cm.$^{-1}$. Also a strong band at 702 cm.$^{-1}$ in the spectrum of vinylene carbonate in solution (715 cm.$^{-1}$ in the liquid state) virtually disappears in the spectrum of the solid. In the polymer of vinylene carbonate the carbonyl doublet disappears, there being only one band at 1833 cm.$^{-1}$ and it is rather surprising that, with the disappearance of unsaturation, the frequency should remain substantially the same as that for the monomer. The band at ~700 cm.$^{-1}$ is also absent in polyvinylene carbonate. It is possible that this band is due to a *cis*-ethylenic out-of-plane :CH deformation mode[27] but the reason for its absence in the solid monomer is obscure.

The carbonyl doublet is also absent from the spectra of propylene carbonate, phenylethylene carbonate and chloromethylethylene carbonate but appears in the case of mono- and di-chloroethylene carbonate. The presence of two absorption peaks in the carbonyl region has been reported for certain halogenated acetic esters and the phenomenon has been ascribed to association.[28] A more likely explanation is rotational isomerism as postulated by Josien and Callas.[29] The boiling point of ethylene carbonate (248°) is abnormally high but that of vinylene carbonate (162°/735 mm.) is more normal.[30] Both

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[23] Kagarise, *J. Amer. Chem. Soc.*, 1955, **77**, 1377.
[24] Thompson and Torkington, *J.*, 1945, 640.
[25] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, p. 156.
[26] Coulson and Moffitt, *Phil. Mag.*, 1949, **40**, 1.
[27] Bellamy, Ref. 25, p. 42. Brown and Sheppard, *Trans. Faraday Soc.*, 1955, **51**, 1611.
[28] McBee and Christman, *J. Amer. Chem. Soc.*, 1955, **77**, 755.
[29] Josien and Callas, *Compt. rend.*, 1955, **240**, 1641.
[30] Newman and Addor, *J. Amer. Chem. Soc.*, 1953, **75**, 1263.

compounds possess high dipole moments.[31, 32] Angell[32a] has recently published a detailed study of the infrared spectra of ethylene carbonate. The disappearance of some of the bands when going from the solid to the liquid (or dissolved) state was interpreted as an indication that the molecule had changed from a non-planar to a planar configuration.

The effects may be associated with differences in dipole–dipole interaction in the two series.

Intense absorption in the region 1300—1000 cm.$^{-1}$ arises from the single-bond C–O stretching vibration in ethers, alcohols, acids, esters, acetals, ketals, etc. This frequency is very sensitive to differences in structural environment.[25] Tschamler and Leutner[33] have shown that in ethers an intense band or double band appears in the range 1250—1000 cm.$^{-1}$ and adjacent unsaturation always shifts the band(s) to higher frequencies. This observation is substantiated generally by Table 4, where the second group of structures has unsaturation adjacent to the C–O link.

TABLE 4.

Type	C–O range, cm.$^{-1}$ (Most intense bands)	Reference
Alkyl ethers	1150—1060	Bellamy,[25] p. 101
Alcohols	1140—1010	,, p. 95
Hemiacetals	1150—1020	Ashdown and Kletz[34]
Carboxylic acids	1320—1210	Bellamy,[25] p. 147
Aryl ethers	1270—1230	,, p. 102
Esters	1245—1185	Thompson and Torkington[24]
Carbonates	1280—1250	Table 2

In the esters two such C–O bonds occur, one contiguous to the carbonyl group and the other between the oxygen and alcohol residue. Thompson and Torkington[24] have assigned the intense band in the region of 1200 cm.$^{-1}$ to the contiguous C–O bond. Other significant bands of somewhat lower intensity and frequency were provisionally assigned to the non-adjacent C–O and to C–C skeletal frequencies. Bellamy (see ref. 25, p. 161) suggests that the carbonyl group stabilises the frequency and intensity of the contiguous C–O bond vibration. Page[35] has also commented on the significance of the contiguous and non-adjacent C–O bonds in the spectra of alkoxy- and acetoxy-steroids and he has identified the band due to the non-adjacent linkage and shown that slight differences exist between the frequencies of axial and equatorial configurations.

In chloroformates, the same distinctions may be drawn between the two C–O bonds. However, examination of the spectral bands in the region 1200—1050 cm.$^{-1}$ for the chloroformates listed in Table 1 shows that it is not always possible to distinguish two bands that could be unequivocally assigned to these two bonds. Methyl formate has its strongest band in the 1250—1050 cm.$^{-1}$ region at 1214 cm.$^{-1}$, falling to 1195 cm.$^{-1}$ in ethyl formate.[24] Methyl chloroformate gives rise to two bands at 1200 and 1147 cm.$^{-1}$, the latter being the more intense, whereas ethyl chloroformate has two bands of comparable intensity at 1160 and 1140 cm.$^{-1}$. In the other chloroformates the main band appears about 1160 cm.$^{-1}$, a substantially lower frequency than might be expected by reference to Table 4 but this shift is due to the inductive effect of the chlorine atom and the introduction of chlorine atoms at the α-carbon atom causes a further shift to lower frequencies (1056 cm.$^{-1}$ in " diphosgene "). While the main band in most cases is probably due to the contiguous C–O bond the origin of the other bands in this region is uncertain.

Bergmann and Pinchas[36] have noted that the normal C–O–C group in ethers, which

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[31] Arbuzov and Shavsha, *Doklady Akad. Nauk S.S.S.R.*, 1949, **68**, 1045.

[32] Slayton, Simmons, and Goldstein, *J. Chem. Phys.*, 1954, **22**, 1678.

[32a] Angell, *Trans. Faraday Soc.*, 1956, **52**, 1178.

[33] Tschamler and Leutner, *Monatsh.*, 1952, **83**, 1502.

[34] Ashdown and Kletz, *J.*, 1948, 1454.

[35] Page, *J.*, 1955, 2017.

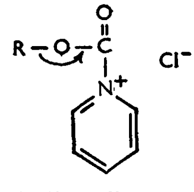
[36] Bergmann and Pinchas, *Rec. Trav. chim.*, 1952, **71**, 161.

absorbs about 1130 cm.$^{-1}$, is split into three or four branches in systems such as acetals and ketals where the two ether groups are linked to the same carbon atom. Repetition of an absorbing substituent on the same central atom is accompanied by a certain amount of coupling and therefore by a shift both towards a higher and a lower frequency than that characteristic for the individual substituent. A similar observation has been made by Page[35] for *gem.*-dialkoxy-steroids. However, in the open-chain carbonate series (Table 2) only one very intense band is found, near 1260 cm.$^{-1}$ in the majority of cases, and the effect of α-chlorine substitution is to shift this to lower frequencies (1178 cm.$^{-1}$ in " diphosgene "). In the cyclic carbonates (Table 3), on the other hand, two strong bands of comparable intensity appear with regularity at about 1160 and 1090 cm.$^{-1}$. Since they are also present in vinylene carbonate we may assume that the C–C frequency is not involved here, and the intensity of the bands points to their both being C–O stretching frequencies. The fact that the higher-frequency band shows quantitative and qualitative shifts relative to the carbonyl band similar to those for open-chain carbonates on introduction of electronegative chlorine atoms suggests that it is the contiguous C–O frequency. However, when the environment alters these two bands shift in the opposite sense in all the compounds shown in Table 3. This would not be expected if the bands represented the two modes, symmetric and asymmetric, of the C–O frequency, since alteration in the force constant would shift both bands in the same direction. It is more likely that the lower frequency band is due to the non-adjacent C–O vibration whose frequency and intensity may be stabilised by the ring form and the absence of free rotation.

No satisfactory explanation has been advanced for the dissociation of " di- " and " triphosgene " into carbonyl chloride; other compounds containing the trichloromethoxycarbonyl group also liberate carbonyl chloride. Nekrassow and Melnikow[37] found that a number of trichloromethyl carbonates readily dissociate to carbonyl chloride and the corresponding chloroformate. Furthermore, they react with alcohols (in excess) and aniline furnishing products that would be derived from a similar reaction with a mixture of carbonyl chloride and the chloroformate. Likewise, " triphosgene " reacts with alcohols to give initially a mixture of alkyl trichloromethyl carbonate and the alkyl chloroformate. Carbonyl chloride is also readily obtained from bistrichloromethyl oxalate.[38] These reactions illustrate the ease of fission of the trichloromethoxycarbonyl group :

$$\mathrm{R{\cdot}CO_2{\cdot}CCl_3} \longrightarrow \mathrm{R{\cdot}COCl} + \mathrm{COCl_2}$$

Alkyl and aralkyl chloroformates, in general, evolve carbon dioxide on strong heating and furnish the corresponding alkyl chloride. This reaction is catalysed by tertiary bases, aluminium chloride, and boron trifluoride.[39-42] Alkyl fluoroformates undergo a similar catalysed decomposition to produce alkyl fluorides.[43] For both catalysed[42] and uncatalysed[44] reactions a mechanism involving initial dissociation into a carbonium ion has been suggested, and the unusual behaviour of phenyl chloroformate (which gives diphenyl carbonate and carbonyl chloride) has been adequately explained in terms of the effect of the phenyl groups. The catalytic effect of pyridine is believed to result from its attack on the carbonyl carbon atom to form the positive charge tending to make the ester bond labile towards displacement by a chloride ion (see inset). Boron trifluoride, analogously gives rise to a similar effect on the alkyl oxygen bond.



Treatment of " diphosgene " with aluminium chloride or ferric chloride induces similar

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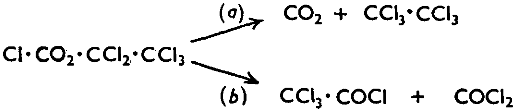
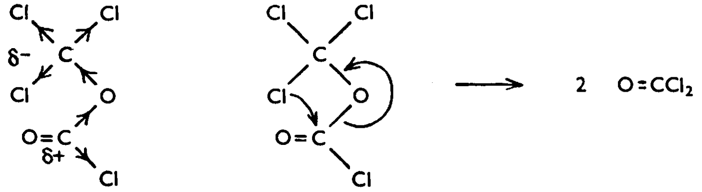
[37] Nekrassow and Melnikow, *J. Gen. Chem., U.S.S.R.*, 1936, **4**, 1057.
[38] Cahours, *Ann. Chim.*, 1847, **19**, 344; *Annalen*, 1848, **64**, 313.
[39] Rennie, *J.*, 1882, **41**, 33.
[40] Carré and Passedouet, *Compt. rend.*, 1935, **200**, 1767.
[41] Carré, *Bull. Soc. chim. France*, 1936, **3**, 1069, 1072.
[42] Nakanishi, Myers, and Jensen, *J. Amer. Chem. Soc.*, 1955, **77**, 5033.
[43] *ibid.*, p. 3099.
[44] Wiberg and Shryne, *ibid.*, p. 2774.

dissociation,[45, 4] which undoubtedly follows a similar course. Perchloroethyl chloroformate [46] also dissociates in two ways :



With aluminium chloride the reaction takes course (*a*) more or less exclusively, while with, *e.g.*, excess of ethyl alcohol the products are ethyl trichloroacetate and ethyl chloroformate, obviously derived by reaction (*b*).

The tendency of the $CO_2 \cdot CCl_3$ group to liberate carbonyl chloride is due to the accumulation of the electronegative chlorine atoms on the carbon atom. In " diphosgene," the inductive effect of the trichloromethyl group is reinforced by that of the chlorine atom attached to the carbonyl carbon atom; the result is to induce a positive charge on the carbonyl carbon atom, and the electrostatic attraction between this and the negative chlorine atom of the trichloromethyl group, which lies in close proximity, promotes the dissociation :



A similar mechanism operates with " triphosgene," alkyl trichloromethyl carbonates, bistrichloromethyl oxalate and perchloroethyl chloroformate.

EXPERIMENTAL

Infrared Absorption Spectra.—These were measured as previously described.[8]

Chloroformates.—Reagent-grade methyl and ethyl chloroformate were purified by fractional distillation. The preparation and properties of chloroformates 3—8 (Table 1), already briefly reported,[47] will be described in a forthcoming publication. Chloroformate No. 5, derived from *trans*-2 : 3-epoxybutane, has been shown to be the (±)-*erythro*-compound; the *trans*-structure has been confirmed for *o*-chloro*cyclo*hexyl chloroformate (No. 7).

" Diphosgene " and " triphosgene " were kindly supplied by the Director, Chemical Defence Research and Development, Ministry of Supply, Porton. The former was purified by fractional distillation in a packed column (glass helices) and the latter by crystallisation from light petroleum (b. p. 60—80°).

1 : 2 : 2 : 2-*Tetrachloroethyl Chloroformate* (*No.* 9) *and Bis*-1 : 2 : 2 : 2-*tetrachloroethyl Carbonate* (*No.* 19).—To a solution of carbonyl chloride (10 g.) in dry benzene (50 g.) were added anhydrous chloral (14·75 g.) and dimethylaniline (12·1 g.). The mixture was set aside overnight; the benzene solution was then washed with 2N-hydrochloric acid and dried ($CaCl_2$), and the benzene removed by distillation. The liquid residue on distillation gave fore-runnings (2·2 g.), b. p. <78°/15 mm., a main liquid fraction (15·5 g.) of 1 : 2 : 2 : 2-tetrachloroethyl chloroformate (Found : C, 14·9; H, 0·7; Cl, 71·3. Calc. for $C_3HO_2Cl_5$: C, 14·6; H, 0·4; Cl, 72·0%), and finally a fraction (4 g.), b. p. 173—175°/15 mm., which formed crystals, m. p. 64° [from light petroleum (b. p. 60—80°)] of bis-1 : 2 : 2 : 2-tetrachloroethyl carbonate (Found : C, 15·5; H, 0·6; Cl, 71·6. Calc. for $C_5H_2O_3Cl_8$: C, 15·25; H, 0·5; Cl, 72·0%). This carbonate was obtained as main product (27 g.) when double the amount of chloral (29·5 g.) was used.

Carbonates.—Commercially available dimethyl, diethyl, and diphenyl carbonates were suitably purified. Carbonates Nos. 13—18 were obtained by reaction of carbonyl chloride

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[45] Ramsperger and Waddington, *J. Amer. Chem. Soc.*, 1932, **55**, 214.

[46] Müller, *Annalen*, 1890, **258**, 50.

[47] " Chemistry Research," 1953. Department of Scientific and Industrial Research, pp. 37—38; 1954, pp. 35—36.

(1 mol.) with the appropriate epoxide (2 mol.).[47] Compound 14 was a mixture of *meso*- and racemic forms which were not separated and, similarly, compound 15 was presumably a mixture of stereoisomers. Bis-2-chloro*cyclo*hexyl carbonate (compound 17) was obtained in two crystalline forms, m. p.s 65—66° and 111°, corresponding to one or other *meso*- and racemic-form of the *trans-trans*-carbonate. Compound 18, which was derived from styrene oxide and carbonyl chloride, had m. p. 51°. This is either the *meso*- or racemic compound; the other form was also obtained but could not be purified by crystallisation.

Ethyl trichloromethyl carbonate (No. 21) was prepared as described by Nekrassow and Melnikow [6] from " diphosgene " and ethyl alcohol. Methyl phenyl carbonate, ethyl phenyl carbonate, and ethyl resorcyl carbonate were prepared by standard methods.

Cyclic Carbonates.—The synthesis of cyclic carbonates by condensation of epoxides with carbon dioxide has been studied by one of us.[47] Ethylene carbonate, propylene carbonate, and chloromethylethylene carbonate were thus prepared. Phenylethylene carbonate was prepared unintentionally while attempting to crystallise ethyl 2-chloro-1-phenylethylcarbamate from moist alcohols. Monochloro- and *s*-dichloro-ethylene carbonate were obtained by chlorination of ethylene carbonate, vinylene carbonate by dehydrochlorination of the mono-chloro-derivative, and the polymer by thermal polymerisation of the monomer with benzoyl peroxide as catalyst.[47] Independently, Newman and Addor,[30] using the same methods, have prepared these last four compounds.

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