Infrared Study of the Surface Reaction of Gaseous Sulphuryl Chloride with Metal Carboxylates

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The surface reaction of metal carboxylates RCO_2M (R = H, Me, Et, Pr^n, and Pr^i; M = Li, Na, and K) with gaseous sulphuryl chloride has been monitored by i.r. spectroscopy. Reactions (I) and (II) take place.

$$2RCO_2M + SO_2Cl_2 \longrightarrow RCOMSO_4 + RCOCl + MCl \quad (I)$$

$$2RCO_2M + SO_2Cl_2 \longrightarrow 2RCOCl + M_2SO_4 \quad (II)$$

Process (I) is observed for all carboxylates except the formates and the lithium salts at 18—30 °C. Sodium acetyl sulphate is formed at room temperature by process (I). After removal of CH_3COCl formed in process (I) and SO_2Cl_2, when the mixture is heated to 150 °C, it reacts further with the carboxylate to give the anhydride and sodium sulphate. In case of potassium acetyl sulphate, when the mixture is heated to 150 °C after the removal of CH_3COCl and SO_2Cl_2, it gives some ester and $K_2CO{\cdot}O{\cdot}SO_3$ in addition to the anhydride. Process (II) occurs for the formates and the lithium salts at room temperature. In the case of the reaction of the formates at room temperature, formyl chloride as the product reacts immediately with sodium and potassium formate to give formic anhydride and with lithium formate to yield formic acid. At 150 °C, all the carboxylates mainly react with sulphuryl chloride according to process (II), and the acyl chloride as product reacts with the carboxylates except the formates to form the anhydride, and the formate to give formic acid. However, in the reaction of potassium acetate at 150 °C, some of the acetyl sulphate as product decomposes with the acetate to give $K_2CO{\cdot}O{\cdot}SO_3$, methyl acetate, and carbon monoxide. This suggests that the process (I) takes place to some extent at 150 °C.

Some sulphuryl chloride reactions take place at moderate temperatures in the presence of aluminium chloride, benzoyl peroxide, or light.[1] In addition, organic compounds such as phenol or polymethoxybenzenes react with sulphuryl chloride at room temperature in the absence of catalysts. This is considered to proceed through ionic or polar forms of sulphuryl chloride.[2]

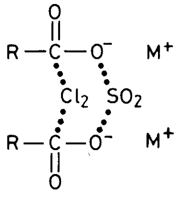
The reactions of sulphuryl chloride have been so far studied for the liquid phase. I report here the surface reaction between sulphuryl chloride and metal carboxylates to help clarify steric and electronic effects at the solid–gas interface. The sulphuryl chloride–sodium acetate system [3-5] was considered to proceed according to reactions (1)—(3). Subsequently, secondary

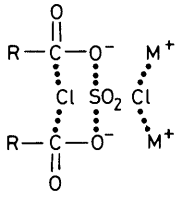
$$2CH_3CO_2Na + SO_2Cl_2 \longrightarrow 2CH_3COCl + Na_2SO_4 \quad (1)$$

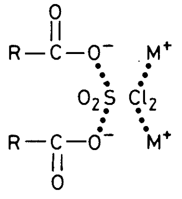
$$2CH_3CO_2Na + SO_2Cl_2 \longrightarrow CH_3COCl + CH_3CONaSO_4 + NaCl \quad (2)$$

$$2CH_3CO_2Na + SO_2Cl_2 \longrightarrow (CH_3CO_2)_2SO_2 + 2NaCl \quad (3)$$

reactions occur and the acid anhydride is formed as final product. For reactions (1)—(3) it is considered that the transitions states (I)—(III) are formed. In this work, the influence of these transition states on the reaction of gaseous sulphuryl chloride with metal carboxylates is discussed.


(I)


(II)


(III)

R = alkyl
M = metal

Experimental

In the reaction of carboxylates with gaseous sulphuryl chloride, a Pyrex i.r. tube (950 ml) was used. A film of alkali metal (Li, Na, and K) was evaporated onto an NaCl plate and the wall of the reaction tube by heating and destroying a small glass tube, in which purified alkali metal was placed, with a tungsten filament at 10^{-5} Torr. A small amount of purified carboxylic acid was degassed, subjected several times to trap-to-trap distillation, and introduced into the i.r. tube equipped with a stopcock. The gaseous acid formed the carboxylate (*ca.* 1.5 mmol) on contact with the alkali-metal film.

The tube was placed in a Hitachi 215 spectrophotometer, evacuated, and heated to 150 °C for 2 h to remove any water and remaining carboxylic acid completely. Then, one of three courses was pursued. In the first, after returning the apparatus to the desired temperature 18—31 or 150 °C, purified sulphuryl chloride (0.652mM) was admitted to the tube and reaction occurred. The i.r. spectra of the thin solid layer of the reacted carboxylate and the gaseous phase were taken at various times. In the second procedure, after reaction by the first route at room temperature, the apparatus was again evacuated for 3 h at room temperature to remove residual gaseous reactants and the gaseous products formed on the successive introduction of sulphuryl chloride (0.39mM), the carboxylic acid (0.874mM), the anhydride (0.39mM), or alternatively, the acyl chloride (0.874mM). The i.r. spectra of

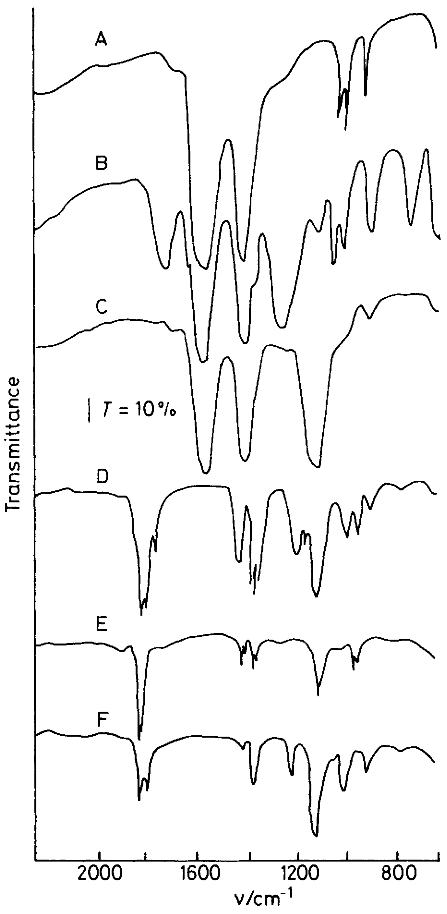


Figure 1. I.r. spectra for the surface reaction of sodium acetate with gaseous sulphuryl chloride at 27 °C: A, solid layer of sodium acetate; B, solid layer 30 min after injection of gaseous sulphuryl chloride (0.652mM); C, solid layer heated to 150 °C after evacuation; D, gas phase after the surface reaction; E, gaseous acetyl chloride at room temperature; F, gaseous acetic anhydride at room temperature

the solid and gas phases were measured for 30 min. In the third procedure, as in the second route, after reaction at room temperature, the apparatus was evacuated for 3 h at room temperature to remove gaseous substances, and then heated to 150 °C after evacuation. The i.r. spectra of the solid and gas phases were obtained by heating and were measured for 30 min at 150 °C. The reaction times at various temperatures for the first route were determined as follows: formates at 18—30 °C, HCO_2Li 30, HCO_2Na 230, HCO_2K 213 min; acetates at 22—28 °C, $MeCO_2Li$ 350, $MeCO_2Na$ 30, CD_3CO_2Na 38, $MeCO_2K$ 20 min; propionates and butyrates at 19—31 °C, $EtCO_2Li$ 51, $EtCO_2Na$ 9, Pr^nCO_2Na 10, Pr^iCO_2Na 10 min; carboxylates at high temperature (60 and 150 °C), HCO_2Li 43 (in this case only at 60 °C), HCO_2Na 32, HCO_2K 13, $MeCO_2Li$ 26, $MeCO_2Na$ 42, $MeCO_2K$ 9 min. At 18—31 °C, the frequencies of the i.r. absorption spectra for each reaction exhibited nearly constant values independent of the temperature. Reaction with sulphuryl chloride was allowed to continue until variation in ν_{asym}(C=O) became negligible. The gaseous products such as acetic anhydride and acetyl chloride were identified by comparing the i.r. spectra with pure samples obtained by g.l.c. (Shimadzu Type GC-6 AM). A 3 × 2 000 mm column (Triton X-305, Chromosorb 101) was used at 70 and 150 °C with a helium flow rate of 40 ml min^{-1}.

Table 1. I.r. frequencies of solid phase for the reaction of gaseous sulphuryl chloride with carboxylates

Reaction	CD_3CO_2Na + SC [a]	$MeCO_2Na$ + SC	$MeCO_2K$ + SC
T/°C	28	150	150
t/min	38	42	9
	ν/cm^{-1}		
	2 320w		
	2 240vw		
	2 160vw		
	1 800sh		
	1 740m		1 730w
	1 560s		
	1 410s		
	1 300sh	1 300vw	
	1 260s		1 270m
		1 150s	1 150s
	1 130m		
		1 100s	1 100s
	1 080w		
			1 040sh
	1 030m		
		1 000vw	1 000sh
	925w		
			900vw
	880w		
	840m		
	830sh		
	790w		760w
	735m		735w

[a] SC = gaseous sulphuryl chloride.

Results and Discussion

As shown in Figure 1A, the i.r. absorption spectra of a thin layer of sodium acetate are measured before reaction. The bands vary greatly for the 30 min after the injection of gaseous sulphuryl chloride at 27 °C. New main bands for the solid phase appear at 1 740, 1 370, 1 260, 1 120, 1 055, 1 005, 900, and 745 cm^{-1} (Figure 1B).

The apparatus was evacuated for 3 h at 27—65 °C after the reaction; however, the intensities and frequencies of the solid-phase bands remain constant throughout evacuation (Figure 1B). Further, when gaseous sulphuryl chloride (0.39mM), acetic acid (0.874mM), or acetic anhydride (0.39mM) was introduced into the reaction tube at 27 °C the solid-phase bands are little affected. However, the intensities of the solid-phase bands of the acetate were decreased on adding gaseous acetyl chloride (0.874mM) at 27 °C, and i.r. absorption bands corresponding to those of acetic anhydride appear in the gas phase. The bands in the solid phase near 1 120 cm^{-1} increase gradually in strength on heating to 150 °C (Figure 1C), and in the gas phase acetic anhydride is mainly formed. The other bands decrease in contrast with the bands near 1 120 cm^{-1}.

After heating, the presence of sulphate ions in the solid phase was ascertained by the usual method. Accordingly, the strong band near 1 120 cm^{-1} is assigned to the degenerate stretching vibration of sulphate ion.[6]

As shown in Figure 1D, the characteristic bands of acetic anhydride appear at 1 820 and 1 770 cm^{-1} [ν (C=O)], and of acetyl chloride at 1 820, 1 800 [ν (C=O)], and 960 cm^{-1} [ν (C–C) + δ (CH_3)].[7] Bonds at 1 430 and *ca.* 1 200 cm^{-1} were from residual sulphuryl chloride and those at *ca.* 1 361 and 1 150 cm^{-1} were assigned to sulphur dioxide[8] from the decomposition of sulphuryl chloride. In the case of the reaction of sodium [$^2H_3$]acetate (Table 1), the bands at 1 740, 1 260, 1 130,

Table 2. Yields of main gaseous products in the reaction of gaseous sulphuryl chloride with carboxylates

Carboxylate used	HCO_2Li	HCO_2Na	HCO_2K	$MeCO_2Li$		$MeCO_2Na$		$MeCO_2K$	
(mmol)	(1.5)	(1.5)	(1.5)	(1.5)		(1.5)		(1.5)	
Sulphuryl chloride used (mM)	0.652	0.652	0.652	0.652		0.652		0.652	
T/°C	R.t.[a]	R.t.	R.t.	R.t.	150	R.t.	150	R.t.	150
t/min	30	230	213	350	26	30	42	20	9
Conversion (%) [b]	20	83	78	38	84	47	100	95	99
Composition of gaseous products (%) [c]									
Formic acid	10.2	t [d]	t						
Formic anhydride		54.2	51.4						
Carbon monoxide	0.2		t						0.7
Sulphur dioxide	9.6	7.5	8.3	18.7	14.8	14.7	18.5	11.1	18.6
Non-reacted sulphuryl chloride	80.0	38.2	40.0	31.3	18.7	35.6		1.4	
Acetic acid				5.0	5.2		6.5		5.5
Acetyl chloride				45.0		27.3		28.9	
Acetic anhydride					61.3	22.4	75.0	58.7	67.0
Methyl acetate									8.2

[a] R.t. = room temperature, 18—31 °C. [b] The conversion was estimated by the $\nu_{asym}(C=O)$ absorbance of the solid carboxylate before and after the reaction. [c] The composition was estimated by i.r. spectroscopy and g.l.c. [d] t = trace.

and 735 cm^{-1} correspond to those of the $MeCO_2Na$ reaction in Figure 1B, and also those for the reaction of $EtCO_2Na$, Pr^nCO_2Na, Pr^iCO_2Na, and $MeCO_2K$. These bands are due to the frequencies of CO and SO groups and are almost independent of the alkyl groups and alkali metal ions. The band near 1 740 cm^{-1} is assigned to ν (C=O) of the acetyl group because the i.r. spectra of acetic acid and its derivatives adsorbed on silica powder are characterized by ν (C=O) 1 760—1 740 cm^{-1}.[9] This band is shifted to higher frequency than the unperturbed frequency due to the interaction between the CO and SO_4 groups in $CH_3CONaSO_4$. Clemett *et al.* reported that ν (C=O) in CH_3COSO_4H is observed at 1 798 or 1 785 cm^{-1} in solution.[10] Since the present ν (C=O) is observed in the solid state, it is considered that the surrounding field effects will contribute to the difference between our frequency and those of Clemmet *et al.*[10] In the case of the reactions of CD_3CO_2M, $EtCO_2M$, Pr^nCO_2M, and Pr^iCO_2M (M = Na and K) with gaseous sulphuryl chloride, the absorption bands near 1 740 cm^{-1} are assigned to ν (C=O) of the acyl groups. In addition, the strong, broad band at 1 260 cm^{-1} is assigned to $\nu_{asym}(SO_2)$ in $CH_3CONaSO_4$. This band is the degenerate stretching frequency of the SO_3^- group in $CH_3COSO_4^-$, and is shifted to a lower frequency than that of the sulphones.[11] However, this is a higher frequency than those of sodium methanesulphonate and ethanesulphonate, 1 202 and 1 193 cm^{-1},[12] showing the effect of the CH_3CO group on $\nu_{asym}(SO_2)$ in $CH_3COSO_4^-$. The bands near 1 120 and 1 055 cm^{-1} correspond to $\nu_{sym}(SO_2)$ in $CH_3COSO_4^-$ as judged by the linear relationship between ν_{asym} and ν_{sym} of the SO_2 group,[13] and by the spectra of the sodium salt of methanesulphonic acid and alkyl trifluoromethanesulphonates.[14] The bands near 1 005 and 745 cm^{-1} (Figure 1B) are assigned to ν (C–O) and ν (S–O) of the C–O–SO_3^- group.

From the i.r. bands, gaseous sulphuryl chloride on reaction with solid sodium acetate initially forms sodium acetyl sulphate, acetyl chloride, and acetic anhydride. The reaction is hindered by an increase in sodium acetyl sulphate concentration, and thus some sulphuryl chloride remains unreacted. The acetyl chloride produced in this reaction reacts further with the residual acetate to give the anhydride. This process also takes place in the reaction of gaseous sulphuryl chloride with carboxylates such as $EtCO_2Na$, Pr^nCO_2Na, and Pr^iCO_2Na at room temperature. A mixture of sodium acetate and acetyl sulphate gives rise to acetic anhydride on heating at 150 °C. On the other hand, gaseous sulphuryl chloride reacts completely with solid acetate in 42 min at 150 °C to form the anhydride and sodium sulphate (Tables 1 and 2). The molar ratios of sodium acetate used and acetic anhydride formed to sulphuryl chloride consumed in the reaction are found to be *ca.* 4 : 1 and 2 : 1. These reactions at room temperature are represented by equation (4). Some RCOCl formed undergoes the secondary reaction (5) with residual RCO_2M. A mixture of $RCOMSO_4$ and RCO_2M reacts on heating at 150 °C as in equation (6). The reaction of gaseous sulphuryl chloride with carboxylates at 150 °C proceeds by equation (7). For reaction (7), two processes are considered. The first forms the anhydride as the final product *via* the steps shown below. Judging from the results of the reaction of potassium acetate at 150 °C (Tables 1 and 2), some acetyl sulphate reacts with the acetate to give $K_2CO{\cdot}O{\cdot}SO_3$ (bands at 1 730, 1 270, 1 150, 1 040, and 735 cm^{-1}), methyl acetate, and carbon monoxide. The second process doesn't follow reaction (4), but occurs through (8) instead, and further gives the anhydride *via* reaction (5). The second process occurs for the reactions of gaseous sulphuryl chloride with the lithium salts ($MeCO_2Li$ and $EtCO_2Li$) and with the formates (HCO_2Li, HCO_2Na, and HCO_2K) at room temperature. The difference between the first and second route can be explained by the two transition states (I) and (II). If the reaction prefers

$$2RCO_2M + SO_2Cl_2 \longrightarrow RCOMSO_4 + RCOCl + MCl \quad (4)$$

$$R = Me, Et, Pr^n, Pr^i$$
$$M = Na, K$$

$$RCOCl + RCO_2M \longrightarrow (RCO)_2O + MCl \quad (5)$$

$$RCOMSO_4 + RCO_2M \longrightarrow (RCO)_2O + M_2SO_4 \quad (6)$$

$$4RCO_2M + SO_2Cl_2 \longrightarrow 2(RCO)_2O + M_2SO_4 + 2MCl \quad (7)$$

$$2RCO_2M + SO_2Cl_2 \longrightarrow 2RCOCl + M_2SO_4 \quad (8)$$

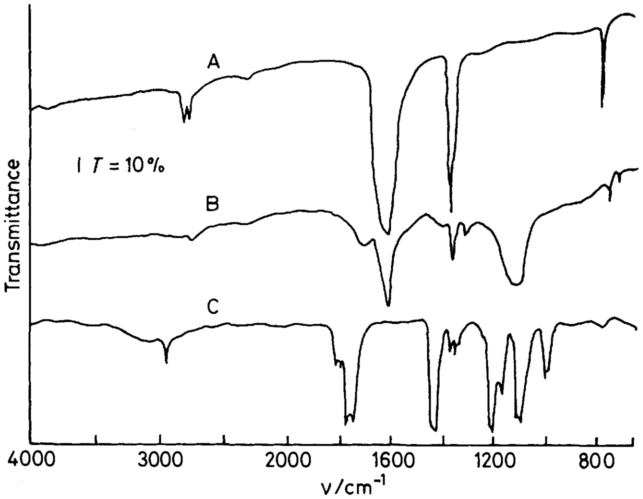


Figure 2. I.r. spectra for the surface reaction of sodium formate with gaseous sulphuryl chloride at 20 °C: A, solid layer of sodium formate; B, solid layer 230 min after injection of gaseous sulphuryl chloride (0.652mM); C, gas phase after the surface reaction

the transition state (II), RCOCl, $RCOMSO_4$, and MCl are first formed in reaction (4), and then the anhydride through reactions (5) and (6). On the other hand, in transition state (I), sulphuryl chloride and carboxylate are first transformed into RCOCl and M_2SO_4 by reaction (8) and RCOCl reacts immediately with RCO_2M in a secondary reaction (5) to give the corresponding anhydride.

Figure 2 shows the i.r. absorption spectra for the reaction of gaseous sulphuryl chloride with solid sodium formate at 20 °C. The bands vary gradually for 230 min after injection of gaseous sulphuryl chloride. The broad band at 1 120 cm^{-1} appears immediately after the start of the reaction and its intensity increases greatly (Figure 2B). As described for the reaction of sodium acetate, the strong, broad band near 1 120 cm^{-1} is assigned to the sulphate ion. New weak bands at 1 720, 1 400, 1 305, and 720 cm^{-1} appear (Figure 2B). These bands are in agreement with those for the solid phase of sodium formate on exposure to gaseous formic acid, and disappear on evacuation. Accordingly, a small amount of formic acid is considered to be formed in the solid phase. As shown in Figure 2C, the bands at 1 820, 1 800, 1 770, 1 755, 1 095, 1 000, and 985 cm^{-1} correspond to formic anhydride[15] and are stable for several hours in dry air or helium at 20 °C.

Upon contact with water vapour, the bands immediately change into those of formic acid. From these i.r. spectra, in the surface reaction of gaseous sulphuryl chloride with solid sodium formate at 20 °C, sodium formyl sulphate is not formed at all, whereas formyl chloride and sodium sulphate are formed immediately. Formyl chloride is rapidly converted into formic anhydride because of its lability.

This process is the same as that of the second path described for the reactions of sulphuryl chloride with acetate at 150 °C [(8) and (5)], and proceeds through the transition state (I). Potassium formate and gaseous sulphuryl chloride at 18 °C react similarly. For lithium formate at room temperature, formic anhydride is not produced at all, while formic acid and a small amount of carbon monoxide are formed (No. 1 in Table 2). Accordingly, reaction (9) first takes place. Subsequently, a secondary reaction occurs to give the anhydride

$$2HCO_2M + SO_2Cl_2 \longrightarrow 2HCOCl + M_2SO_4 \quad (9)$$

from the sodium or potassium salt and formic acid from the lithium one. The occurence of another process is indicated by the fact that the yield of carbon monoxide is smaller than that of formic acid at room temperature (Table 2) and CO_2 and SO_2 are formed to a substantial degree at 150 °C.

In conclusion, gaseous sulphuryl chloride and solid alkali-metal carboxylates react through the two transition states (I) and (II), in which there is an interaction between the electrophilic sulphur atom of sulphuryl chloride and nucleophilic oxygen of the carboxylates.

For formates there is a lowering of the steric hindrance on the solid surface and an enhanced positive charge on the carbon atoms of the carbonyl groups compared with the other esters. Accordingly, gaseous sulphuryl chloride is converted into HCOCl and M_2SO_4 through the transition state (I).

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