# Formation of New Products in a Solid-Solid Reaction in the Presence of Organic Solvent Impurity

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(Received: April 12, 2011; Accepted: June 17, 2011)

### ABSTRACT

We discuss the formation of new products in a solid – solid reaction in the capillary as in well as in bulk in the presence of an organic solvent impurity in a small amount. Three reactions namely KI + HgCl<sub>2</sub>, Cul + HgCl<sub>2</sub> and Agl + HgCl<sub>2</sub> were studied. It was found for some of the organic solvent impurities, a small amount of some substance appeared in the half occupied by HgCl<sub>2</sub>. Thus it became clear that some of the organic substances were reacting with HgCl<sub>2</sub> to produce a new substance which be an organo-metallic product. In this light HgCl<sub>2</sub> was made to react with the different solvents. However, the new product could be separated out only in two cases, with Cyclohexanone and Dimethylsulfoxide. A black coloured product was formed with Cyclohexanone and with Dimethylsulfoxide the new product of a light greenish colour. With the other solvents like Acetophenone and Nitrobenzene, the product, if formed, could not be separated out. So a preliminary study of the two products naming these as product A is formed by the reaction of Cyclohexanone solvent with HgCl<sub>2</sub> and product B is formed by the reaction of Dimethylsulfoxide solvent with HgCl<sub>2</sub> both at 80°C, for 5 hours. The preliminary studies carried out were measurement of molecular weight (by elevation of boiling point method), ionicity, XRD, FTIR etc.

Key words: New products, organic solvents, molecular weight, ionicity, XRD and FTIR.

#### INTRODUCTION

Many solid-solid capillary reactions have been studied during the last many years e.g 1-4. In the studies normally carried out so for, both the solid reactants do not have any impurities. The main motivation of the earlier work, including that of the senior author (R.A.) in this field was to obtain a better understanding of the reaction mechanism of solid-solid reactions.eg 2,5 Introduction of simple organic impurities was a step in this direction. While studying the solid-solid capillary reactions in the presence of small amounts of some organic solvent impurity, that a small amount of some substance appeared in the half occupied by one of the reactants. Thus it became clear that some of the organic substances were reacting with one of the

reactants to produce a new substance which be an organo – metallic product.

Here, we discuss the formation of new products due to the presence of an organic solvent impurity in a small amount. The reactions studied are  $KI+HgCl_2$ ,  $CuI + HgCl_2$  and  $AgI + HgCl_2$  in the presence of small amount of organic solvent impurity.

The two reactants when packed side by side in a capillary tube of a narrow diameter, say 0.5 cm after moistening with different solvent impurities and kept in an oven maintained at  $80^{\circ}$ C showed some new product on HgCl<sub>2</sub> side in two cases.

In the light of the indication from capillary studies HgCl, was made to react with the different solvents. However, the product could be separated out only in two cases, with Cyclohexanone and Dimethylsulfoxide. A black coloured product was formed with cyclohexanone and with Dimethylsufloxide the new product was of a light greenish colour. With the other solvents like Acetophenone and Nitrobenzene, the product, if formed could not be separated out. So, we have made a preliminary study of the two new products, naming these as product A and product B respectively. The product A is formed by the reaction of Cyclohexanone solvent with HgCl<sub>2</sub> and product B is formed by the reaction of Dimethylsufloxide solvent with HgCl<sub>2</sub>, both at 80°C, for 5 hours.

### **EXPERIMENTAL**

#### Method of preparation

We take 4 gms of well ground HgCl<sub>2</sub> (99.9% Merck) reactants, moistened with about 0.4 ml of Cyclohexanone solvent (99% Merck) on a watch glass. Then it is put in an oven at constant temperature of 80° C, for 5 hours. In this way,a black coloured product is formed,this is called product A Same procedure is adopted for the Dimethylsulfoxide solvent (99% Merck). HgCl<sub>2</sub> is moistened with 0.4 ml of the double distilled solvent and the same procedure is followed in this case also. A light greenish coloured product is formed, this is called product B. Powdered crystals of the new products are taken for observation, measurement and other studies with simple techniques for finding out their physical properties etc. These are given in Table 1.

# Measurement of Molecular weight (By elevation of boiling point method)

The equation relating the boiling point elevation with the molecular weight of the solute is given as <sup>e.g.6</sup>.

$$M_{2} = \frac{1000 W_{2} K_{b}}{W_{q} T_{b}}$$

where  $M_2$  is the molecular weight of the solute,  $W_2$  is the mass of solute,  $K_b$  is the molal elevation constant,  $W_1$  is the mass of the solvent and  $T_b$  is the boiling point elevation due to the presence of the solute. THF is used as solvent.

S. No.	Property	Name of solvent	Product A	Product B
	Topolty			
1.	Solubility	i) THF	Soluble(0.140gm/ml)	Soluble(0.097gm/ml)
		ii) DMSO	Slightly soluble	Slightly soluble
		iii)Cyclohexanone	Slightly soluble	Slightly soluble
		iv)Acetophenone	Slightly soluble	Slightly soluble
		v)Acetone	Slightly soluble	Slightly soluble
		vi) Benzonitrile	very slightly soluble	Very slightly soluble
2.	Density		5.20 gm/cm <sup>3</sup>	4.90 gm/cm <sup>3</sup>
3.	Melting Point		Above 250°C	Above 250°C

#### Table 1: Physical properties of new products

# Table 2: Result of the measurements of the molecular weight of the products with Thf as solvent

S. No	Compound obtained	Experimental Molecular Weight
1.	HgCl <sub>2</sub>	272.54
2.	Product A(with Cyclohexanone)	284.07
3.	Product B(with DMSO)	303.25

 $\rm T_{\rm _b}$  is measured by a digital electronic thermometer.

Benzoic acid and Acetanilide are taken as standard solute. A known small amount of the solute is added to known amount of THF solvent and the elevation of boiling point is found out. All chemicals used are 99% purity Merck chemicals.

The  $K_b$  occurring in the formula for the determination of molecular weight is found out using Benzoic acid and Acetanilide as solute. The mean value of  $K_b$  using Actanilide as solute is used for the determination of molecular weight. The mean value

of  $\rm K_{\rm b}$  for THF is 191.45. These molecular weights are given in Table 2.

# Measurement of some other properties of this new product such as ionicity, XRD, FTIR etc

The kinetics of the reaction is studied by placing 400 mgms of  $HgCl_2$  and about the same amount of Cul in close contact near the middle, first without any impurity, and then after mixing with the two new products formed, as impurities, taken turn by turn. Both the reactants are 99.9% purity Merck chemicals. The internal diameter of the pyrex glass tube is 0.5 cm and about 5 cm length. These

Angle [ 20]	d-value α1 [Aº]	d-value α2 [A°]	Peak intensity (counts)	Relative intensity [%]
20.335	4.3635	4.3744	246	100.0
21.620	4.1070	4.1172	83	33.6
24.860	3.5786	3.5875	21	8.6
25.375	3.5071	3.5158	20	8.2
26.350	3.3795	3.3879	90	36.6
28.035	3.1801	3.1880	23	9.3
29.085	3.0676	3.0753	40	16.1
29.415	3.0340	3.0415	86	35.1
29.875	2.9883	2.9957	174	70.7
33.125	2.7022	2.7089	130	52.7
37.230	2.4131	2.4191	69	27.9
41.390	2.1797	2.1851	61	24.7
42.415	2.1293	2.1346	69	27.9
43.860	2.0625	2.0676	41	16.6
45.225	2.0033	2.0083	100	40.6
46.835	1.9382	1.9430	42	17.1
47.830	1.9001	1.9049	49	19.9
50.945	1.7910	1.7955	55	22.2
51.570	1.7708	1.7752	16	6.5
52.185	1.7513	1.7557	14	5.9
55.085	1.6658	1.6699	26	10.6
56.900	1.6169	1.6209	23	9.3
57.885	1.5917	1.5957	12	4.7
58.275	1.5820	1.5859	20	8.2
60.195	1.5360	1.5399	20	8.2
62.980	1.4746	1.4783	21	8.6
64.025	1.4531	1.4567	18	7.2
66.490	1.4051	1.4085	19	7.9

# Table 4: XRD of Pure HgCl,

are kept in an air thermostat oven, controlled upto 0.5° C to 1°C at 80°C. The product thickness is measured with a traveling microscope having a least count of 0.01mm at equal intervals of time (15 min). The results are given in Fig. 1 and the corresponding digital data are given in Table 3.

The X-ray diffractogram of HgCl<sub>2</sub> and the two products are obtained. These are given in Figs. 2-4. The corresponding digital data are given in Tables 4-6. The digital data of some of the most prominent diffraction peaks is given in Table 7. The near – matching normal mode frequencies of HgCl<sub>2</sub> and the two products are given in Table 8 (a) and the remaining

ones are given in Table 8 (b). The FTIR spectrum of  $HgCl_2$  and the two products are given in Figs. 5-7.

### DISCUSSION

We see from Table 7 that the prominent peaks of product A are very nearly at the same place as that of  $HgCl_2$ . This means that  $HgCl_2$ molecule remains more or less as such in product A, with some organic group getting attached to the  $HgCl_2$  molecule, consistent with the molecular weight of product A. This proposal is consistent with observations because the organic group is expected to diffract X-rays very-very scantily.

Table 5: XRD of product A

Angle [ 2θ]	d-value α1 [A°]	d-value α2 [A°]	Peak intensity (counts)	Relative intensity [%]
20.32	4.36692	4.3704	380	100.00
21.612	4.10868	4.1120	135	35.53
24.815	3.58514	3.5880	40	10.53
25.357	3.5097	3.5126	35	9.21
26.311	3.3845	3.3873	130	34.21
27.938	3.19103	3.1936	70	18.42
28.095	3.17667	3.1762	60	15.79
29.018	3.07467	3.0772	60	15.79
29.394	3.03622	3.0387	110	28.95
29.871	2.98879	2.9912	195	51.32
33.06	2.70737	2.7096	130	34.21
37.196	2.41527	2.4173	80	21.05
38.08	2.36122	2.3632	30	7.89
39.217	2.29537	2.2972	30	7.89
41.012	2.19892	2.2008	40	10.53
42.418	2.12923	2.1310	80	21.05
43.81	2.06477	2.0665	95	25.00
45.191	2.00484	2.0065	80	21.05
46.207	1.96308	1.9647	40	10.53
46.769	1.94079	1.9424	60	15.79
47.785	1.90187	1.9034	45	11.84
50.903	1.79244	1.7939	55	14.47
55.11	1.66515	1.6665	45	11.84
56.84	1.61852	1.6198	35	9.21
57.745	1.59528	1.5966	35	9.21
60.139	1.53738	1.5386	40	10.53
62.978	1.47473	1.4759	40	10.53
65.241	1.42893	1.4301	30	7.89
66.514	1.40465	1.4058	40	10.53

On the other hand, for product B, the 100% intensity is diffracted for d=8.0289 which is a totally new d-value. Also there is a new peak of 34.8% intensity at d=3.4618. There is also a new peak of intensity 15% at d=2.7696. Rest of the prominent

d values for product B are more or less same as for  $HgCl_2$  From this, we may conclude that at least one chlorine is replaced by an organic group consistent with the observed molecular weight. This should account for the observed X-ray data.

Angle [ 2θ]	d-value α1 [Aº]	d-value α2 [Aº]	Peak intensity (counts)	Relative intensity [%]
6.186	14.27593	14.2880	160	27.83
9.854	8.96856	8.9762	80	13.91
11.011	8.02892	8.0355	575	100.00
11.723	7.54304	7.5490	70	12.17
13.327	6.63857	6.6438	90	15.65
16.855	5.25601	5.2603	70	12.17
18.039	4.91365	4.9176	90	15.65
18.729	4.73396	4.7380	70	12.17
20.362	4.35795	4.3615	200	34.78
21.674	4.09704	4.1004	80	13.91
22.133	4.01315	4.0164	70	12.17
23.283	3.81737	3.8205	100	17.39
24.959	3.56474	3.5677	150	26.09
25.42	3.50005	3.5040	185	32.17
25.79	3.46176	3.4546	200	34.78
26.385	3.37518	3.3780	70	12.17
28.413	3.13874	3.1413	110	19.13
29.494	3.02616	3.0286	70	12.17
29.905	2.98542	2.9879	150	26.09
31.415	2.8453	2.8477	50	8.70
32.297	2.7696	2.7719	90	15.65
33.066	2.70692	2.7091	80	13.91
34.047	2.6311	2.6333	80	13.91
34.945	2.56556	2.5677	65	11.30
35.984	2.49383	2.4959	60	10.43
37.229	2.41324	2.4152	60	10.43
41.232	2.18771	2.1895	100	17.39
42.367	2.13168	2.1334	70	12.17
43.254	2.09003	2.0917	50	8.70
43.858	2.0626	2.0643	70	12.17
45.184	2.00511	2.0068	75	13.04
46.809	1.93921	1.9408	50	8.70
47.653	1.90684	1.9084	50	8.70
48.39	1.87951	1.8810	40	6.96
50.472	1.80673	1.8082	40	6.96
51.002	1.78919	1.7907	50	8.70
53.02	1.72578	1.7272	40	6.96
61.437	1.50796	1.5092	40	6.96

# Table 6: XRD of product B

From Table 8 (a), we also notice many near matching between the normal mode frequencies of  $HgCl_2$  and those of product A. There are fewer near matching between the frequencies of  $HgCl_2$  and those of product B. This is consistent with our proposal regarding the new products.

We may tentatively suggest the following structures for the new products. Then one should have a very close look at the FTIR and other supporting data to eliminate many of the proposed structures to hopefully arrive at the best choice.

S.	Pure	HgCl <sub>2</sub>	Product A		Produc	t B
No.	ds	۱%	ds	1%	ds	1%
1.					8.0289	100
2.	4.3635	100	4.3669	100	4.3579	34.8
3.	4.1070	33.6	4.1087	35.5	4.097	13.0
4.	3.5786	8.6	3.5851	10.5	3.5647	26.0
5.	3.5071	8.2	3.5097	9.21	3.5000	32.2
6.	3.4618	34.8				
7.	3.3795	36.6	3.3845	34.2	3.370	12.0
8.	3.0340	35.1	3.0362	28.9	3.026	12.0
9.	2.9883	70.7	2.9888	51.3	2.9854	26.0
10.					2.7696	15.0
11.	2.7022	52.7	2.7074	34.2	2.7069	13.0
12.	2.0033	40.6	2.0647	25.2	2.0051	13.0

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Tab	le 8	(b)	):
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Table 8(a):

S.No.	Product A	Product B	S.	FTIR of Pure	Product A	Product B
1.		674.52	No.	HgCl <sub>2</sub>		
2.		708.54	1.	467.69	464.62	459.58
3.	743.37		2.	1021.2	1026.39	
4.		897.89	3.	1080.42		
5.		831.30	4.	1184.56	1184.0	
6.		952.22	5.	1458.34	1445.94	1427.19
7.		1310.80	6.	1612.76	1611.64	1611.91
9.		1348.06	7.	1916.02	1915.98	
10.		1401.57	8.			1976.85
11.		1478.80	9.	2855.16	2851.54	
12.	1703.05		10.			2908.03
13.		2046.72	11.	2926.16	2924.12	
14.		2259.18	12.	3195.01		
15.		2259.18	13.	3525.8	3524.48	3524.49
16.		2331.27	14.	3585.37	3583.5	3583.19
17.	2357.24	2365.41	15.	3932.47		3922.43
18.		2908.03				
19		2997.91				
20.	3889.39					



Fig. 4: X- Ray diffractogram of Product B



Fig. 7: FTIR of product B

Proposed structure of the new product being given here merely as one of the	Formula weight Weight	Observed Molecular	to arrive at t of the FTIR being done	
examples			Th solvents, Cy	
Product A (HgCl <sub>2</sub> )CH <sub>3</sub> SHO	287.54	287.07	be seen fro are noted in	
Product B Hg SHO	299.54	303.25		

The above are merely examples and these are not even good examples. Out of the many proposals, that one may make, one should be able to arrive at the correct structure, mainly on the basis of the FTIR and other supporting data. That is not being done here.

The normal mode frequencies of the two solvents, Cyclohexanone and Dimethylsulfoxide can be seen from Fig. 8 and 9, where the frequencies are noted in digital form over the spectrum.

# **Concluding Remark**

One structure for product A and one for product B are tentatively proposed. More such structures have to be proposed and assessed



Fig. 8: FTIR of Cyclohexanone



Fig. 9: FTIR of Dimethylsulfoxide

against the observed molecular weighty and the spectra etc. Only then one may arrive at a unique structure for each of the two products.

# ACKNOWLEDGEMENTS

We wish to express our thanks to Prof. M.A. Wahab, HOD Department of Physics, JMI, New Delhi for X-ray measurement. Thanks are also due to Prof. Kamaluddin, Department of Chemistry, IIT Roorkee for X-ray and FTIR measurements. We would also like to thank Prof. Amir Azam for FTIR measurements. Special thanks are due to the Ex-Head of the Chemistry Department Prof. Kishwar Saleem, for extending to us the facilities of the Department. We are also thankful to Prof. Sharif Ahmad, Head Department of Chemistry, JMI, New Delhi.

### REFERENCES

- Beg M.A., Ansari S.M., J. Solid State Chem. 20: 103 (1977).
- Beg M.A., Saud R., Ind. J. Chem. 25A: 373 (1986).
- Beg M.A., Jain A., *Polyhedron* 11(21): 2775 (1992).
- 4. Beg M.A., Ansari S.M., J. Solid State Chem.

18: 57 (1976).

- 5. Rahman R., Ph.D. Thesis, Aligarh Muslim University, Aligarh (1984).
- Maron S.H. and Prutton C.F., Principles of Physical Chemistry, 4<sup>th</sup> ed, Amerind Publishing Co. New Delhi, Bombay, Calcutta, New York (1965).