

better than for any other rate law which was tried. Agreement of the k 's within single runs is illustrated by Table II; the runs selected are the two marked with an asterisk in Table I. The falling off of k toward the end of each run is hardly surprising, since every one of the three

sources of error in the pressure readings—formaldehyde polymerization, phosgene formation and the thermal reaction—would tend to cause just such an apparent decrease.

The authors would like to express their thanks to Prof. T. D. Stewart and to Dr. D. B. Luten, Jr., for assistance in devising a method for the identification of formyl chloride.

Summary

The photochemical reaction between chlorine and formaldehyde takes place in two steps. The first is an exothermic, long-chain process involving no pressure change. It is accompanied by a marked Draper effect, and under certain conditions may become explosive. One of its products is formyl chloride, COHCl, a semi-stable substance which decomposes in the second step of the reaction into carbon monoxide and hydrogen chloride. The decomposition takes place by a rapid chlorine-sensitized photochemical process if chlorine is in excess, and by a slow heterogeneous thermal reaction if no chlorine is available or if illumination is stopped.

Formyl chloride may be prepared from chlorine and formaldehyde by allowing an illuminated mixture to flow through a liquid air trap. The substance is stable at liquid air temperatures, but decomposes fairly rapidly when brought to room temperature.

BERKELEY, CALIFORNIA

RECEIVED JULY 11, 1934

TABLE I

Initial CH ₂ O, cm.	Initial Cl ₂ , cm.	Final Cl ₂ , cm.	COHCl, cm.	Pressure change in 10 sec., cm.	k
15.9	19.7	3.8	10.0	1.1	0.92
9.8	14.0	4.2	4.8	1.1	1.20
9.8	14.0	4.2	5.8	1.2	1.19
*16.0	21.6	5.6	9.3	2.4	1.40
10.0	16.0	6.0	6.5	1.4	0.92
14.7	20.9	6.2	8.0	2.3	1.31
16.1	22.4	6.3	11.6	2.6	1.21
15.9	23.1	7.2	7.2	2.5	1.29
14.7	22.1	7.4	8.0	2.0	0.96
*23.6	31.0	7.4	13.2	3.8	1.40
14.6	22.6	8.0	9.9	2.5	0.99
21.2	29.3	8.1	14.7	3.4	1.10
11.7	22.3	10.6	5.6	3.7	1.47
16.1	36.4	20.3	11.2	5.7	0.84

TABLE II

Press. change in 10 sec., cm.	A		Press. change in 10 sec., cm.	B	
	COHCl, cm.	k		COHCl, cm.	k
2.4	9.3	1.40	3.76	13.2	1.40
2.2	7.0	1.48	3.18	9.7	1.38
1.8	5.0	1.44	2.12	6.8	1.36
1.2	3.5	1.15	1.90	4.5	1.21
0.9	2.4	1.04	1.22	3.0	0.95

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Weighing of Molybdenum as Silver Molybdate

BY LEROY W. McCAY

In a study of the interaction of hydrogen sulfide and molybdic acid, an investigation which has engaged the attention of the writer for a number of years, the need arose for a quick and accurate method for determining the amount of molybdenum in alkali molybdates. For this purpose the precipitation and weighing of molybdenum as silver molybdate has proved to be most convenient.¹ Since the salt is slightly soluble in water a determination of its solubility was made. It was found that 100 cc. of water at 25° dissolve

0.0044 g. of Ag₂MoO₄ (average of four closely agreeing results). It was further found that in water containing a moderate amount of silver nitrate the solubility is practically nil.

The alkali molybdate was dissolved in about 150 cc. of water, a drop of methyl orange solution added and drop by drop enough sulfuric acid to render the liquid just red. A gram of crystallized sodium acetate was then dissolved in the solution, it was heated to boiling, the flame removed and a solution of silver nitrate added slowly with constant stirring until the yellowish-white precipitate, which soon became curdy, had settled sufficiently to leave the solution clear enough to test if more silver nitrate was necessary to complete the precipitation of the molybdenum. While cooling, the solution was stirred thoroughly off and on so that when it had reached room temperature the liquid

(1) According to Smith and Bradbury silver molybdate and silver tungstate are unsuitable forms in which to weigh molybdenum and tungsten, for both salts are very soluble and decompose on heating (*Ber.*, **24**, 2934 (1891)).

above the precipitate was quite clear. Sometimes the precipitate was filtered off at once, and sometimes after twenty-four hours. The clear liquid was poured through a Neubauer crucible (to avoid the use of a filter paper) and the precipitate transferred to the crucible with a minimum amount of a dilute solution of silver nitrate (5 g. of the salt in 1000 cc. of H_2O). It was washed seven to eight times by letting from 4–5 cc. of the wash-solution flow from a pipet around the upper rim of the crucible and then drawing it off with the pump. The small amount of silver nitrate remaining in the precipitate was washed out with 15 cc. of 96% alcohol, 5 cc. being used each time. Finally, after removing the alcohol as thoroughly as possible with the pump, the precipitate was dried to constant weight at 110° . At this temperature it still contained traces of water (0.0003 g., average of many determinations), and a further heating to 250° was necessary. This was carried out as follows. A large porcelain crucible of about 75-cc. capacity was adjusted 11 cm. above the top of a Bunsen burner and a 550° thermometer clamped upright with its bulb in contact with the bottom of the crucible. By regulating the length of the burner flame the desired temperature could be obtained roughly. When the temperature was reached and remained constant the thermometer was removed and the Neubauer crucible introduced. During the heating the precipitate became pink and then purple in color, which slowly disappeared above 250° and was completely discharged at 350° .² The disappearance of the purple color was not accompanied by any perceptible change in weight of the precipitate. During all the operations care was taken to protect the precipitate from direct sunlight.

(2) Smith and Bradbury (*loc. cit.*) noticed this purple color. Their statement that the salt when moderately heated melts to a clear, yellow liquid is not in accord with the experience of the writer, who finds that the liquid is purple and on cooling solidifies to a yellowish-white mass.

1. Seven samples of Merck blue label ammonium molybdate ranging between 0.2642 and 0.5104 g. were analyzed and, when corrected for traces of water in the Ag_2MoO_4 dried at 110° , gave an average value of 54.40% Mo, with an average deviation of 0.02% and a maximum deviation of 0.08%. Calcd.: Mo, 54.36%. Found by the ignition method: Mo, 54.43%.

2. Three determinations next were made in another sample of Merck blue label salt, which by the ignition method gave 54.48% Mo. Found: Mo (average), 54.47%. The course of procedure was exactly that given above.

3. Some sodium molybdate which had lost a part of its water of crystallization was recrystallized and carefully dried. Found in it by ignition 14.82% H_2O ; calculated, 14.87% H_2O . Five determinations of the molybdenum in this recrystallized salt averaged 39.69%, the lowest result being 39.65% and the highest 39.75%. The theoretical percentage is 39.67. Nothing is gained by dissolving the precipitate in nitric acid and titrating the silver according to Volhard. The solution goes on too slowly—indeed, is only complete when the acid has been heated for some time. The results, however, are satisfactory.

For the determination of molybdenum in alkali molybdates the method is easier and more expeditious than are those of Berzelius–Rose (precipitation as Hg_2MoO_4) and Chatard (precipitation as $PbMoO_4$).

Summary

It has been shown that the molybdenum in alkali molybdates can be determined easily and accurately by converting them into silver molybdate, which while slightly soluble in water is practically insoluble in water containing silver nitrate.

PRINCETON, NEW JERSEY

RECEIVED JULY 12, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

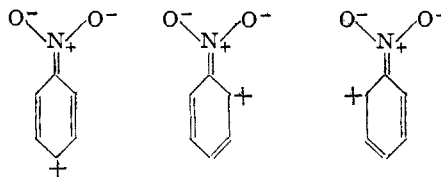
Dipole Moments and Molecular Structure of Amides

BY W. D. KUMLER AND C. W. PORTER

The fact that certain groups of atoms have different moments when attached to the benzene ring than when attached to aliphatic radicals has been ascribed to the inductive and electromeric effects of the benzene ring.¹ Resonance involving essentially the same idea as electromerism gives perhaps a more precise picture of this phenomenon. In many cases the structure of a molecule is not one definite form, but a combination of several electromeric configurations. The large moments of most simple aromatic compounds as compared with the corresponding simple aliphatic compounds are due, in part, to the contributions

made by excited forms in which certain atoms are positively charged and others are negatively charged.

In nitrobenzene the excited forms



contribute appreciably to the structure of the molecule and these excited forms raise the moment of the aromatic compound considerably above that of an aliphatic nitro compound in

(1) Sutton, *Proc. Roy. Soc. (London)*, **133A**, 668 (1931).