stirred for three hours at 25°. The reaction mixture was filtered and the filtrate acidified with *N* hydrochloric acid. The precipitate was collected, washed, dried ***in vacuo***, and recrystallized from 30% ethanol to give 1.7 g. (93%) of III, colorless needles, m. p. 186–187°.

Anal. Calcd. for $C_{15}H_{11}O_5NI_2 \cdot H_2O$ (557): C, 32.4; H, 2.4; N, 2.5. Found: C, 32.5; H, 2.7; N, 2.3.

3,5-Diiodo-4-(3',5'-diiodo-4'-hydroxyphenoxy)-hippuric Acid (IV) —To 0.7 g. of III, dissolved in 10 ml. of 15 *N* ammonium hydroxide, was added, slowly and with stirring, the requisite amount of *N* potassium triiodide. When about half of the iodine had been added, the ammonium salt of IV separated in the form of glistening silvery leaflets. After all of the iodine had been added the solution was stirred for several minutes and allowed to stand at 5° for three to four hours. The suspension was decolorized with sodium metabisulfite and the free acid liberated by the addition of acetic acid. The precipitate was collected, washed with water, and dried ***in vacuo*** to give 1.0 g. (97%) of IV, colorless crystalline powder, m. p. 248° with decomposition and evolution of iodine. After recrystallization from 70% ethanol IV was obtained as colorless leaflets, m. p. 248° with decomposition.

Anal. Calcd. for $C_{15}H_9O_5NI_4$ (791): C, 22.8; H, 1.1; N, 1.8. Found: C, 22.8; H, 1.5; N, 1.8.

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GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY
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The Light Absorption and Fluorescence of Triarylmethyl Free Radicals

BY LINUS PAULING

By working at low temperatures with triarylmethyl free radicals frozen in a rigid glassy solvent, Lewis, Lipkin, and Magel[1] have obtained absorption spectra and fluorescence spectra which show a striking vibrational fine structure, essentially the same for absorption (determined by the vibrational structure of the excited state) and fluorescence (determined by the normal state); the authors report nine vibrational frequencies for the triphenylmethyl radical, and their reproduced microphotometer records indicate one or two more (Table I).

TABLE I

COMPARISON OF VIBRATIONAL FREQUENCIES

Triphenylmethyl		Benzaldehyde
Absorption	Fluorescence	Raman
190	230	239 cm^{-1}.
(400)[a]		439
600	670	615
820		827
970	970	1001
1090	1080	1164
		1203
1520	1550	1597
	1850	
	2210	
	2510	
		3063

[a] Estimated from the published microphotometer record.

It may be noted that an interesting correlation exists between these absorption and fluorescence spectra of triphenylmethyl and the Raman spectra of substituted benzenes. The principal Raman frequencies of substituted benzenes are 200, 400, 615, 1000, 1165, 1595, and 3060 cm.$^{-1}$; all but the last (the carbon–hydrogen stretching frequency) are represented in the absorption and fluorescence spectra. The correlation is closest with monosubstituted benzenes containing a group conjugated with the benzene ring, such as methyl benzoate and benzaldehyde; Raman frequencies for benzaldehyde (other than the carbonyl frequency 1700 cm.$^{-1}$) are given for comparison in Table I. There is a rough correlation in intensity as well as in frequency.

The bands at 1850, 2210, and 2510 may be combinations or overtones; they may well be combinations of the important frequency 1550 cm.$^{-1}$ with lower frequencies. The failure of the band with shift 3063 cm.$^{-1}$ to appear in the fluorescence spectrum may indicate that the coupling of this C–H vibration with the electronic transition is very weak.

An interesting detail is the gradual change in shape of the absorption spectrum in the 1000–1200 cm.$^{-1}$ region as the phenyl groups in the triphenylmethyl radical are successively replaced by *p*-*t*-butylphenyl groups. The band at 1000 cm.$^{-1}$ gradually diminishes in intensity, and finally disappears; the spectrum of tri-(*p*-*t*-butylphenyl) methyl, which otherwise closely resembles that of triphenylmethyl, shows a single peak at 1120 cm.$^{-1}$ in place of the 970–1080 doublet. This fact is without doubt related to the observed characteristic absence of the lines near 1000 cm.$^{-1}$ in the Raman spectra of the para-disubstituted benzenes.

I believe that measurements of well-resolved absorption spectra, fluorescence spectra, and phosphorescence spectra of rigid solutions at low temperatures may provide much useful information about the vibrational frequencies of molecules of dyes and other substances which could not be readily obtained by the techniques of Raman and infrared spectroscopy.

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PASADENA, CALIFORNIA RECEIVED OCTOBER 4, 1944

The System Sodium Molybdate–Sodium Nitrate–Water and Part of the System Sodium Molybdate–Molybdic Oxide–Water, at 25°

BY J. E. RICCI AND L. DOPPELT[1]

The experimental procedure for these measurements was that described for similar investigations of ternary systems of salts and water. The materials used were C. P. products throughout, the molybdic oxide being a very pure sample,[2] found

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(1) G. N. Lewis, D. Lipkin, and T. T. Magel, THIS JOURNAL, **66**, 1579 (1944).

(1) Present address: U. S. Army.

(2) This material, resublimed and of stated purity 99.97%, was the gift of the Climax Molybdenum Company.

to be 99.9+ % MoO_3 by alkalimetry and by weighing as lead molybdate.

The results of the equilibrium measurements for the system Na_2MoO_4–$NaNO_3$–H_2O at 25° are given in Table I. In this system the liquids were analyzed for sodium molybdate by means of the Volhard method, titrating excess of silver ion with standard thiocyanate after precipitation and filtration of silver molybdate from neutral solution. Since no mention was found in the literature of the application of the indirect Volhard method to the determination of molybdate,[3] the procedure was first tested on known samples of sodium molybdate, and was found to be accurate to about one part per thousand, and hence adequate for the purpose. The total solid was determined by evaporation of separate samples, giving the sodium nitrate content by difference. A few densities are listed, determined by using calibrated pipets, fitted with filter paper, in the sampling of the saturated solutions for analysis.

TABLE I

SYSTEM Na_2MoO_4–$NaNO_3$–H_2O AT 25°

Original complex		Saturated solution			
Wt.% Na_2MoO_4	Wt.% $NaNO_3$	Wt.% Na_2MoO_4	Wt.% $NaNO_3$	Density	Solid phase
...	0.0	39.42	0.0	1.430	$Na_2MoO_4 \cdot 2H_2O$
50.75	5.43	33.28	8.09		$Na_2MoO_4 \cdot 2H_2O$
47.83	8.09	30.34	11.95		$Na_2MoO_4 \cdot 2H_2O$
44.16	12.45	25.93	18.07		$Na_2MoO_4 \cdot 2H_2O$
43.91	15.98	21.20	24.82		$Na_2MoO_4 \cdot 2H_2O$
35.88	23.97	15.16	34.23	1.446	$Na_2MoO_4 \cdot 2H_2O$
33.95	29.10	14.31	35.48	1.452	$Na_2MoO_4 \cdot 2H_2O + NaNO_3$
19.93	44.97	14.41	35.40	1.452	$Na_2MoO_4 \cdot 2H_2O + NaNO_3$
12.99	48.01	14.54	35.21	1.454	$Na_2MoO_4 \cdot 2H_2O + NaNO_3$
Average	...	14.42	35.36	1.453	$Na_2MoO_4 \cdot 2H_2O + NaNO_3$
9.96	55.01	14.28	35.46	1.455	$NaNO_3$
7.99	54.09	10.74	38.46	1.434	$NaNO_3$
4.00	55.03	5.03	43.44	1.405	$NaNO_3$
0.0	...	0.0	47.87	1.389	$NaNO_3$

The results given show that these salts form neither solid solutions nor double compounds and that the sodium molybdate at this temperature exists as a dihydrate, in equilibrium with its aqueous solution. The separate solid phases of this system were clearly identified by the algebraic extrapolation of the ternary tie-lines which, in the case of the molybdate, converged at the composition of the dihydrate with an average error of ±0.18% in terms of $NaNO_3$. These results agree with the work of Funk,[4] who studied the binary system Na_2MoO_4–H_2O, determining the transition temperature for the phases $Na_2MoO_4 \cdot 10H_2O$–$Na_2MoO_4 \cdot 2H_2O$ to be 10–11°.

The solubility here reported for $Na_2MoO_4 \cdot 2H_2O$ at 25°, 39.42%, density 1.430, is the average of three runs, and was determined both from undersaturation and from supersaturation. The value is a little lower than that interpolated from Funk's solubility curve for the same temperature (39.61%), but agrees with the value (39.4%) reported by Bye for 24°.[5]

Table II lists the results of the study of a small part of the system Na_2MoO_4–MoO_3–H_2O at 25°, in the region of high concentrations of sodium molybdate. These complexes reached equilibrium more and more slowly the higher the molybdic oxide content. The time required ranged from about a week for the first few points shown in Table II, to over two months for the last two points. With the exception of number 11, equilibrium was established in every case by the constancy of the composition of the saturated liquid solution upon repeated analysis. Complex number 11 seems to have developed the correct solid phase, as shown by its tie-line, but the liquid composition had not become constant, and it does not fall exactly on the smooth solubility curve connecting all the other points.

TABLE II

PART OF SYSTEM Na_2MoO_4–MoO_3–H_2O AT 25°

	Original complex		Saturated solution		Solid phase	
No.	Wt.% Na_2MoO_4	Wt.% MoO_3	Wt.% Na_2MoO_4	Wt.% MoO_3	Formula	% H_2O by extrapolation
1	...	0.0	39.42	0.0	$Na_2MoO_4 \cdot 2H_2O$	
2	47.40	2.60	39.50	.00	$Na_2MoO_4 \cdot 2H_2O$ + $Na_2Mo_2O_7 \cdot 6H_2O$	
3	43.10	4.10	39.46	.00		
	Average	..	39.48	.00		
4	39.70	4.74	38.78	.00	$Na_2Mo_2O_7 \cdot 6H_2O$	23.7
5	38.94	4.94	37.66	.00	$Na_2Mo_2O_7 \cdot 6H_2O$	21.8
6	38.01	5.21	36.66	.010	$Na_2Mo_2O_7 \cdot 6H_2O$	23.9
7	37.90	5.20	36.38	.00	$Na_2Mo_2O_7 \cdot 6H_2O$	22.4
8	35.79	5.99	33.44	.026	$Na_2Mo_2O_7 \cdot 6H_2O$	21.9
9	35.05	6.10	32.54	.018	$Na_2Mo_2O_7 \cdot 6H_2O$	22.3
10	33.72	6.19	30.85	.047	$Na_2Mo_2O_7 \cdot 6H_2O$	22.2
11	32.28	6.77	28.81	.083	$Na_2Mo_2O_7 \cdot 6H_2O$	23.3
12	29.92	8.10	24.82	.320	$Na_2Mo_2O_7 \cdot 6H_2O$	23.2

The analysis of the Na_2MoO_4–MoO_3 solutions involved the titration of the free molybdic acid with standard sodium hydroxide, using phenolphthalein as indicator, in one sample, and the determination, in a second sample, of the total solid by evaporation. In connection with this latter determination it was found that while the two solid components could easily be dried to the anhydrous state, with constant weight, separately, by evaporation at 100°, followed by one hour at 300°, this was not the case for mixtures of the two solids. The combinations did not give up their water completely even after prolonged heating at 300°, the effect increasing with increasing proportion of molybdic oxide in the mixture. This stubborn retention of water may indicate the formation of some hydrated polymolybdate stable at 300°. Gentle ignition on a small free flame for about thirty minutes, however, gave complete drying without measurable volatilization of molybdic oxide; the residues were therefore so treated for short periods, to constant weight. The entire procedure for the combined analysis was verified on prepared mixtures of known composition, and the accuracy was found to be of the order of one or two parts per thousand. A similar difficulty is reported by Bye,[5] who states that the determination of total solid by evaporation is exact only if the composition of the residue lies between that of the dimolybdate and that of the tetramolybdate.

As the table shows, addition of any molybdic oxide to the system causes the formation of a second solid phase, a hydrated dimolybdate, so that the solubility curve for solutions saturated

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[3] L. W. McCay recommended the precipitation of silver molybdate as a gravimetric determination of molybdate; THIS JOURNAL, **56**, 2548 (1934).

[4] Funk, *Ber.*, **33**, 3696 (1900).

[5] Bye, *Bull. soc. chim.*, **10**, 239 (1943).

with the normal molybdate is practically nonexistent in the system Na_2MoO_4–MoO_3–H_2O at 25°. The isothermally invariant solution in equilibrium with both solid phases is in fact practically coincident with the point representing the aqueous solubility of the pure normal molybdate. This solution contained no detectable concentration of molybdic oxide, and had the composition, therefore, of 0.00% MoO_3 and 39.48% Na_2MoO_4.

The second solid phase listed in Table II, the hydrated dimolybdate, was a fine white solid which settled slowly to form a milky mass. By graphical estimation of the intersection of the tie-lines in this region, it was evident that the solid was either the hexa- or the pentahydrate of $Na_2Mo_2O_7$. The intersections of these tie-lines with the line representing the ratio of Na_2MoO_4 to MoO_3 corresponding to the dimolybdate, were calculated by suitable simultaneous equations, in terms of the percentage of water at the point of intersection (last column of Table II). The nine tie-lines involved gave an average water content for the solid phase of 22.7%, to be compared with the theoretical values of 23.60 for the hexahydrate and 20.47 for the pentahydrate. These results show the hexahydrate to be the more probable formula, but they cannot be called conclusive.

This salt was reported as hexahydrated by Rosenheim,[6] who presented analytical figures in support of it, and as pentahydrated by Frey (Soubarew-Châtelain),[7] with no supporting data. Bye,[5,8] most recently, again gives the hexahydrate formula, as established by analysis of the separated solid phase and by the method of wet residues; no experimental data for either of the methods, however, are given in his article. The present observations may be taken as adding evidence for the formula of the salt as a hexahydrate.

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(6) Rosenheim, *Z. anorg. allgem. Chem.*, **96**, 143 (1916).

(7) Frey (Soubarew-Châtelain), *Compt. rend.*, **211**, 503 (1940); **208**, 1153 (1939).

(8) The article by Bye (ref. 5), reporting an almost complete study of the system Na_2O–MoO_3–H_2O at 24°, and including therefore the portion of the system Na_2MoO_4–MoO_3–H_2O here described, came to our attention only after the present article was written and, in fact, ready for printing.

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Measurement of the Rate of Reaction of Potassium Iodide with Organic Chlorides in Dilute Acetone Solution

BY KENNETH L. SENIOR, RICHARD R. HETRICK AND JOHN G. MILLER

Recently[1] the rates of reaction of certain organic chlorides with potassium iodide in dilute acetone solution were measured by the analytical procedure based on the Andrews titration method as established for such reactions by Conant and co-workers.[2] At dilutions where the total concentration of reactants was less than 0.125 molar, the specific rates showed an irregular increase in value with increasing dilution. This behavior could not be attributed satisfactorily to salt or medium effects. Although the possibility of interference by acetone in the titration was recognized, this appeared unlikely especially in view of the constancy of each specific rate value measured over a wide range of reaction times.

Further investigation of the problem is reported here, using benzyl chloride as organic chloride. The same behavior of the specific rate values was obtained, when using the Andrews procedure, as reported in the previous study.

The reliability of the analytical procedure was then tested by analyzing a carefully prepared solution of potassium iodide by the Andrews, the permanganate,[3] and the Volhard methods. In the absence of acetone the results for each of the methods, run in triplicate, were within 0.1% of the theoretical. On repeating the analyses with addition of various amounts of acetone, the results obtained with the Andrews and permanganate methods varied as much as 25% from the theoretical, even though the values obtained by these two methods were in close agreement. The presence of acetone did not cause any appreciable error in the Volhard method.

While no complete study was made of the nature of the interference by the acetone, it was evident that a large part of the acetone dissolves in the chloroform and that when the acetone is present in large amount the sensitivity of the chloroform layer as an indicator for free iodine is impaired. Thus the end-point of the Andrews titration, shown by the absence of iodine color in the chloroform layer, is reached too soon and in the rate measurements a low estimate of the amount of unreacted iodide is obtained, causing an erroneous and high value of the specific rate. For higher iodide concentrations the error will be negligible and there the method has proved successful in rate studies. The irregularity in the behavior of the specific rate values for the dilute solutions is probably due to the differences in the amount of acetone present in the samples titrated and the differing concentrations of the iodate solutions used.

The interference of the acetone was further demonstrated by using the aqueous layer as an indicator. It had been observed that after the chloroform layer had become colorless, the water layer still showed a fleeting brownish-yellow color of iodine upon addition of more iodate or permanganate. Taking the point at which further addition of iodate produced no fleeting brownish-yellow color in the aqueous layer as the end-point gave specific rate values which were in very

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(1) Skolnik, Day and Miller, THIS JOURNAL, **65**, 1858 (1943).

(2) Conant and Kirner, *ibid.*, **46**, 232 (1924); Conant and Hussey, *ibid.*, **47**, 476 (1925).

(3) Kolthoff, Laitinen and Lingane, *ibid.*, **59**, 429 (1937).