These results cannot be explained until some method is found of separating the adsorbed and unabsorbed dye on the fiber.

The optical method indicates that there is an actual solution of the dye in the fiber. The next step in explaining the mechanism of dyeing must be to find some method which will separate the dissolved dye from that held on the fiber by adsorption.

Summary

A study of the absorption spectra of light reflected from dyed materials showed that the reflection spectra more nearly explained the variations in color between two dyes than the transmission spectra of the solutions.

Dyeings made on wool, paper and gelatin indicated that the dye was present as a solution in these materials.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY COLLEGE OF SCIENCE OF CALCUTTA]

THE TEMPERATURE OF EXPLOSION FOR ENDOTHERMIC SUBSTANCES. II. TRINITRO-META-CRESOLATES AND THEIR EXPLOSION TEMPERATURES

BY RASIK LAL DATTA, LOKNATH MISRA AND JOGENDRA CHANDRA BARDHAN

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The temperature of explosion has already been studied in the case of a few typical organic compounds, namely, nitro-bodies, picrates, azo compounds, haloid compounds, organic perchlorates, alkaloids, etc.[1] All of these classes of substances are endothermic and hence give explosion temperatures. Previous to our investigations, the explosion temperatures of a very few substances which explode before melting or decomposing were known and for endothermic substances generally such a temperature was never before known to exist. Several of the endothermic substances were, because of their practical use as explosives, known to explode by means of detonators and some of these were shown by Berthellot[2] to explode when thrown into a vessel previously raised to a high temperature.

The object of these investigations is to show that endothermic substances in general give an explosion temperature, and how the temperature varies according to the endothermic properties and molecular grouping. The reason why such an important constant has previously escaped detection is that substances which either melt or decompose at temperatures below the explosion temperature could not at all attain that temperature in the ordinary course of heating. The temperature is known only for those substances which explode before they are decomposed or volatilized.

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[1] Datta and Chatterjee, *J. Chem. Soc.*, **115**, 1006 (1919). Previous communication on the subject.

[2] Berthellot, *Compt. rend.*, **105**, 1159 (1887); **129**, 926 (1899).

This is clearly evident when we examine how Silberrad and Phillips[3] did not obtain the explosion temperatures of trinitrophenol and its ammonium, hydrazine and mercury salts, while they were successful with all the stable metallic salts of trinitrophenol which do not decompose or volatilize before the temperature of explosion is reached. The trinitrophenol is decomposed and the ammonium and hydrazine salts volatilized before the temperature of explosion is attained. This temperature can be determined in air, or in an atmosphere of inert gas such as carbon dioxide and nitrogen or in a vacuum. The method of determination as described in the previous communication on the subject was to drop small quantities of the substances to the bottom of a clean test-tube immersed in a bath of potassium hydrogen sulfate just when the temperature particular to each substance had been attained. The extreme accuracy and reliability of this temperature as an important physical constant for all endothermic substances will be evident from the practical determination of the explosion temperature of acenaphthene-trinitro-*m*-cresolate. This test was performed at 5°-intervals from 350° to 450° without explosion, but at 455° the substance exploded. The bath was cooled, and tests were made at 445° and 450° without explosion, but at 452° explosion occurred. The bath was again cooled and tests made at 448° and 450° without explosion, but at 451° explosion occurred. Once more the bath was cooled and a test made at 450° without explosion, but at 451° explosion again took place. It is thus evident that the temperature of explosion is sharp and quite accurate; the explosion at 451° was marked by a vivid flash of light.

The temperature of explosion should be of great value in determining the purity of endothermic substances which do not give either a melting or a boiling point, since it has been found that the explosion temperature is elevated markedly in the presence of traces of moisture and other impurities. A perfectly pure substance gives the correct explosion temperature, just as it gives correct boiling and melting points.

Furthermore, this constant should be of great practical importance in the manufacture of explosives. It is generally a fact that the lower the temperature of explosion, the easier the substance is exploded and hence the smaller the charge of detonator needed. By determining the explosion temperature of a given explosive, the charges of detonator which would be necessary to explode it satisfactorily may be found at once by comparison with a known explosive having a similar temperature of explosion; no practical tests whatever should be necessary.

Experimental Part

In Table I are listed the names, formulas, properties, analyses, and explosion temperatures of 19 compounds with trinitro-*m*-cresol. The

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[3] Silberrad and Phillips, *J. Chem. Soc.*, **93**, 475 (1908).

TABLE I

PREPARATION AND PROPERTIES GF TRINITRO-META-CRESOLATES

Compound	Formula	Cryst. from	Color and form	M. p. °C.	Analyses						
					Subs. G.	N_2 Cc.	Conditions °C.	Conditions Mm.	N Calc. %	N Found %	Expt. temp. °C.
Acenaphthene	$C_{12}H_{10}.T_2$[a]	alc.	yellow feathers	120	0.0363	4.3	30	758	13.13	13.04	451
Fluorene	$C_{13}H_{10}.T$	bz.	deep yellow needles	109	0.1049	10.2	30	753	10.27	10.64	421
Allylamine	$3C_3H_7N.T$	alc.-bz.	shining yellow	165	0.0556	9.9	23.5	766	20.27	20.32	265
					0.5067	10.1	24	765		20.44	
Benzylamine	$C_7H_9.N.T$	H_2O	gold-yellow needles	185	0.1206	17.4	30	760	16.00	16.06	406
Camphylamine	$C_{10}H_{19}N.2T$	H_2O	lemon-yellow needles	183	0.0648	8.7	23	766	15.33	15.48	391
Menthylamine	$C_{10}H_{21}N.2T$	H_2O	lemon-yellow needles	200 decomp.	0.0710	9.5	22.5	766	15.29	15.34	410
Piperazine	$2C_4H_{10}N_2.T$	alc.-H_2O(1:3)	lemon-yellow needles	220–225 decomp.	0.0691	15.0	31	757.5	23.61	23.79	359
α-Naphthylamine	$C_{10}H_9N.T$	H_2O	dirty yellow needles	165–170 decomp.	0.0771	10.0	30	754	14.51	14.32	470
p-Chloro-aniline	$C_6H_6NCl.2T$	H_2O	lemon-yellow needles	170–172	0.0696	10.0	26	760	15.98	16.12	449
p-Bromo-aniline	$C_6H_6NBr.2T$	aq. alc.	lemon-yellow gran.	172.5	0.0593	8.0	30	763	14.89	14.95	441
p-Iodo-aniline	$C_6H_6NI.2T$	dil. alc.	bright yellow needles	152	0.0913	11.4	34	761	13.98	13.70	466
o-Anisidine	$C_6H_4(OCH_3)NH_2.T$	alc.	pale yellow needles	178 decomp.	0.1040	14.3	32	760	15.30	15.18	349
o-Phenetidine	$C_6H_4(OC_2H_5)NH_2.T$	alc.	bright yellow needles	165	0.1294	17.0	24	764	14.73	14.89	385
Hexamethylenetetramine	$(CH_2)_6N_4.T$	alc.-bz.	....	175	0.0336	8.0	36	760	25.58	25.88	325
Pseudo-cumidine	$C_6H_2(CH_3)_3NH_2.2T$	alc.	velvety yellow needles	183 decomp.	0.0646	9.0	28	760	15.78	15.63	477
Triphenylguanidine	$(NHC_6H_5)_2CNC_6H_5.T$	alc.	brilliant yellow prismatic needles	182	0.0608	8.65	32	760	15.84	15.71	454
Dimethyl-α-naphthylamine	$C_{10}H_7N(CH_3)_2.T$	bz.	hard, brilliant plates	154	0.1101	13.8	28	760	13.52	14.06	358
α-Naphthol	$C_{10}H_8O.T$	dil. alc.	orange-yellow silky needles	159	0.1288	13.4	30	754	10.83	11.24	472
β-Naphthol	$C_{10}H_8.T$	dil. alc.	orange needles	124	0.0685	7.2	30	753	10.83	11.42	452

[a] T = $C_6H(CH_3)(OH)(NO_2)_3$.

compounds with acenaphthene, fluorene, allylamine, benzylamine, *p*-chloro-aniline and dimethyl-α-naphthylamine were obtained by mixing hot saturated solutions of the constituents and allowing the mixtures to cool slowly.

Camphylamine and α-naphthylamine were dissolved in dil. hydrochloric acid and mixed with hot saturated solutions of trinitro-*m*-cresolate in water. The menthylamine and piperazine derivatives were prepared from hot aqueous solutions. *p*-Bromo-aniline was dissolved in water and added hot to an alcoholic solution of the cresol, while alcohol was used for both solutions in the cases of *p*-iodo-aniline, *o*-anisidine, *o*-phenetidine, pseudocumidine, triphenyl-guanidine and α-naphthol. The hexamethylenetetramine and β-naphthol compounds were prepared by mixing hot aqueous solutions.

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Summary

The temperature of explosion of an endothermic organic explosive substance is a natural constant.

Addition compounds between 19 aromatic amines and phenols and trinitro-*m*-cresol have been prepared and their explosion temperatures determined.

CALCUTTA, INDIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

STUDIES ON CELLULOSE CHEMISTRY

IV. PROPERTIES OF GAMMA-DELTA-DIHYDROXY-CARBONYL DERIVATIVES AND THEIR BEARING ON THE POLYMERIZATION OF POLYSACCHARIDES

BY HAROLD HIBBERT AND JOHN ARREND TIMM[1,2]

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The suggestion was made by one of us some years ago[3] that cellulose was probably derived from an anhydro glucose of the type of Formula I and this was termed the cellulose nucleus.

In a later paper[4] a comprehensive review was made of the reactions to which any formula for cellulose must conform and opportunity was taken to emphasize the importance of the role played by the hydroxyl groups in the γ,δ positions to the —CHO radical.

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[1] This paper is constructed from Part II of a dissertation presented by John Arrend Timm in June, 1922, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

[2] Communicated to the Cellulose Section, American Chemical Society, Birmingham, Alabama, April, 1922.

[3] Hibbert, *Chem. Met. Eng.*, **22**, 838 (1920).

[4] Hibbert, *J. Ind. Eng. Chem.*, **13**, 256, 334 (1921).