of the solvent was removed under reduced pressure without heating, the residue, after being treated with petroleum ether (20 ml.), gave crystals weighing 0.6 g. Further recrystallization from carbon tetrachloride petroleum ether gave colorless prisms, m.p. 100–102°. The analysis indicated that this material was α-bromodesoxyphenetoin (II).

Anal. Calcd. for $C_{18}H_{19}O_3Br$: Br, 22.00. Found: Br, 21.87.

(B) A mixture of I (0.3 g.) and bromine (0.2 g.) in carbon tetrachloride (3 ml.) was warmed on a water bath until the solvent had evaporated. The residue was crystallized from ethanol (3 ml.), yielding halogen-free compound (0.2 g.). Repeated recrystallization from ethanol gave colorless needles, m.p. 151–153°, which failed to depress the melting point of authentic phenetil.

Phenetoin. A mixture of II (0.4 g.; 0.001 mole) and sodium ethoxide [sodium (0.07 g.; 0.003 mole) in 3 ml. of absolute ethanol] was allowed to stand overnight at room temperature. Then it was poured into water and neutralized with cold 10% hydrochloric acid. Resulting precipitates were collected, washed with water, and dried (0.3 g.). Twice recrystallized from ethanol, the compound had m.p. 88–89°, reported m.p. 86–87°.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.04; H, 6.58.

1,2,2-Trianisylethanone. (A) Trianisylbromoethylene (0.6 g.) was heated with 20 ml. of 50% ethanol in a sealed tube at 100° for 24 hr. After the supernatant fluid was removed, the oily residue was treated with 10 ml. of absolute ethanol denatured with 1% anisole, giving colorless prisms (0.4 g.), which melted at 74–76° to a cloudy liquid and became clear at 79°. Reported[8] m.p. for *1,2,2-trianisylethanone anisolate,* 77–79°.

(B) To a cooled solution of α-bromodesoxyanisoin (1.1 g.) and anisole (1.1 g.) in carbon disulfide (30 ml.), pulverized aluminum chloride (2 g.) was added in small portions with stirring (30 min.), and the mixture was allowed to stand at room temperature for 20 hr. Upon decomposition of the complex in ice and concentrated hydrochloric acid, a viscous yellow liquid was obtained from the organic layer. This could be crystallized from the same solvent as employed in the former case, the crystals thus obtained (0.6 g.) showing no depression of melting point when mixed with the material described under A.

The reduction of the anisolate with sodium borohydride in methanol gave 1,2,2-trianisylethanol, m.p. 107–108°; reported[9] m.p. 107–108°.

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CHEMICAL LABORATORY
KITASATO INSTITUTE
TOKYO, JAPAN

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The Color Produced in Acetone Solutions of Nitroaromatics and Sodium Iodide

RICHARD W. SHELLMAN[1]

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It was recently reported by Blatt and Gross[2] that aromatic nitro compounds and alkali iodides in acetone solution develop colors in the visible region which can be used as a qualitative test for aromatic nitro compounds and the number of nitro groups they contain: Acetone solutions approximately 0.1*M* with respect to both the aromatic nitro compound and sodium iodide are very pale yellow if the aromatic nitro compound contains one nitro group; deeper yellow, comparable with the color of 0.3*M* aqueous iron (III) chloride, if the aromatic nitro compound contains two nitro groups; and red-brown, comparable with the color of 3.0*M* aqueous iron (III) chloride, if the aromatic nitro compound contains three nitro groups.

The only earlier report of the color reaction in question is that of Tronow, D'yakonova-Schultz, and Zonova,[3] who examined three trinitro- and two dinitroaromatics, varied the solvent and inorganic iodide widely, and concluded from indirect evidence that the acetone complexes had the probable composition, one aromatic nitro compound: one alkali iodide: three acetone.

EXPERIMENTAL

Reagents and apparatus. 1,3-Dinitrobenzene (DNB) was recrystallized from ethanol until a product with a constant melting point of 90.5–91.5° (uncorr.) was obtained. As a test for water-soluble impurities, a small amount of the product was shaken with distilled water and then filtered. The water was unchanged in *p*H, and tests for nitrate and nitrite were negative. 2,4,6-Trinitrotoluene (TNT) was recrystallized from ethanol until a constant melting point of 80.5–81.5° (uncorr.) was obtained. An earlier observation[4] that TNT when exposed to light develops a red impurity was confirmed. The red color (corresponding to an absorption centered at about 510 mμ) develops more quickly in solutions of TNT in acetone than it does in the dry solid. Solid TNT in a brown bottle can be kept for several weeks without appreciable decomposition; when the red color does develop, it can be removed by one or two recrystallizations. 4,4'-Dinitrobiphenyl, recrystallized from acetone, had a melting point of 241–242° (uncorr.). Mallinckrodt Analytical Reagent acetone was used as solvent without further purification. Mallinckrodt Analytical Reagent sodium iodide was dried at 110° overnight and weighed from a weighing bottle. (Sodium iodide was selected rather than potassium iodide because of its higher solubility in acetone.)

Spectrophotometric measurements were made on a Beckman model DK-1 recording spectrophotometer.

1,3-Dinitrobenzene. 1,3-Dinitrobenzene absorbs strongly in the ultraviolet region of the spectrum. Since this absorption is centered at wave lengths at which acetone is opaque, the measurements in acetone solution were made along the side of the absorption curve. Addition of sodium iodide moves the absorption toward longer wave lengths corresponding to the appearance of the yellow color, and the cut-off becomes much less sharp. (See Figure 1.) The region between about 420 mμ and 550 mμ appeared to be the most fruitful region for study, for at these wave lengths the mixture solutions absorb strongly whereas the solutions of either reactant alone are transparent or nearly so.

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(1) Present address: Department of Chemistry, The Ohio State University, Columbus 10, Ohio.

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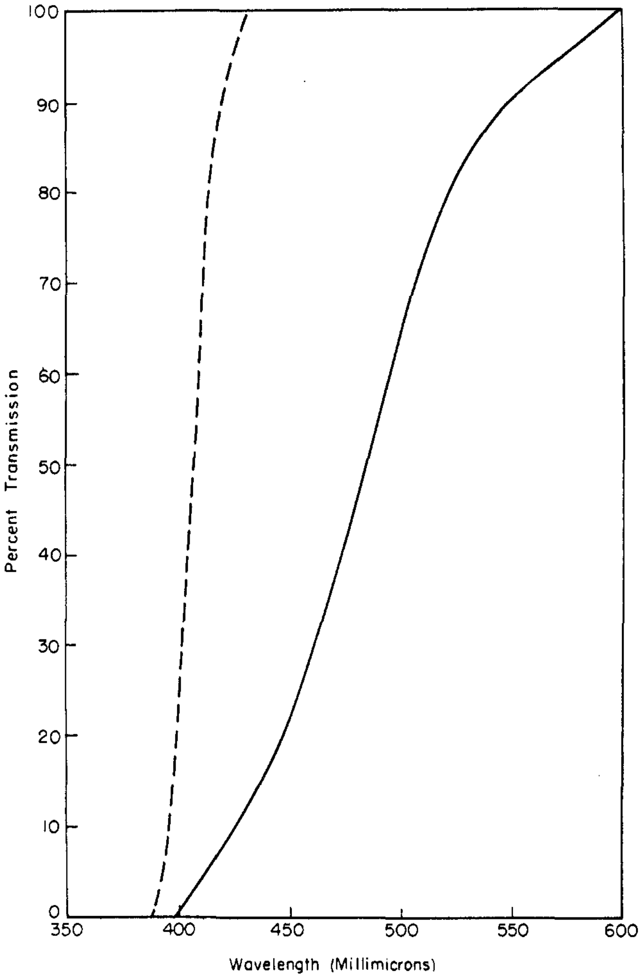

FIG. 1. ABSORPTION SPECTRA OF ACETONE SOLUTIONS 0.05M in 1,3-dinitrobenzene (broken line) and 0.05M in 1,3-dinitrobenzene and in sodium iodide (solid line). Path length 1 centimeter

The method of continuous variations[5,6] was used in an attempt to establish the molecular combining ratio of the two reactants. In two different experiments, one starting with 0.05M reactants and the other with 0.1M reactants, taking several different wave lengths each time, curves were obtained which peaked near $X = 0.5$, indicating a molecular combining ratio of 1:1. The curves of enhancement versus combining ratio were quite rounded, indicating a rather unstable complex.

The ratio 1:1 was checked by a method which we might call the "method of effect of excess."[7,8] Application of this method to the 1,3-dinitrobenzene and sodium iodide mixtures gave results which confirm the 1:1 ratio indicated by the continuous-variations data. The formula will therefore be written NaI·DNB, without any assumptions for the present as to its detailed structure. The complex does not obey Beer's Law, and the deviation is in the direction which would be expected for a complex that dissociates on dilution.

2,4,6-Trinitrotoluene. A similar study was undertaken to establish the combining ratio between 2,4,6-trinitrotoluene and sodium iodide. Both the continuous-variations (using original solutions of 0.02M and of 0.1M) and the effect-of-excess methods indicate a 1:1 combining ratio in this system also. This compound will therefore be formulated as TNT·NaI.

4,4'-Dinitrobiphenyl. The method of continuous variations was then tried on 4,4'-dinitrobiphenyl and sodium iodide. For original solutions in acetone of concentration of 0.04M a 1:1 complex is indicated for this system also. More concentrated solutions were not used because the solubility of 4,4'-dinitrobiphenyl is low.

Effect of water. It was observed that the colors resulting in acetone solution from nitroaromatics and iodides were bleached by the addition of relatively small amounts of water. This effect was quantitatively studied by spectrophotometry. The drop in absorbance is greatest for the first added increments of water. For example, at 450 mμ an acetone solution 0.050M in NaI and in DNB (1 cm. path length) was observed to have an absorbance of 0.66. With the same concentrations of NaI and DNB but with 1.1 mole liter^{-1} of water in the acetone solution the absorbance is 0.350, and at 5.6M water it is 0.117. Similar results are obtained with TNT and NaI.

When the acetone solutions which had water as well as sodium iodide and 1,3-dinitrobenzene in them were allowed to stand for several days, they gradually took on a purple hue corresponding to the appearance of a new absorption centered at 560 mμ. This new absorption develops most rapidly in the solutions having the most water. The solutions containing no added water maintain the yellow color for long periods of time.

Effect of alkali. The sodium iodide which was used contains some alkaline material, for its concentrated aqueous solutions have a pH of between 8 and 9. To determine whether the color might be due to this alkaline constituent, a qualitative experiment was conducted using dilute aqueous solutions of sodium hydroxide and of sodium carbonate. It was found that small amounts of these basic reagents, when added to acetone solutions of the nitroaromatics, had the same effect as equal amounts of water. When larger amounts were added, deeply colored solutions (blue-violet for DNB, cherry-red for TNT) were produced. These colors have been observed previously and have been used for estimation of the amount of nitro compound.[9] The spectra of these solutions show marked similarities as would be expected from the close relationship between the nitro compounds. In each case there are two absorption maxima, with the maximum of shorter wave length being the stronger in each case. The wave lengths of the maxima are 465 mμ and 535 mμ for TNT and 570 mμ and 700 mμ for DNB. The 570 mμ absorption observed here may be the same as the 560 mμ absorption observed in wet acetone solutions of sodium iodide and DNB. Differences in the ionic strength of the solution may be sufficient to account for the small difference in the wave length of the absorption maximum.

The belief that these absorptions are due to the same species is strengthened by the observation that, while the purple color is formed instantly on the addition of relatively large amounts of strong base (sodium hydroxide), the addition of the weaker base sodium carbonate or of very small amounts of sodium hydroxide results in a slower formation of the purple color. (The time required ranges from several minutes to several hours.) With sodium iodide, as noted above, development of the color requires one or more days—which is consistent with the observation that the sodium iodide reagent is only very slightly basic. The presence of at least a small amount of water seems to be

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required for formation of the colors. Canback[10] has suggested that the colored species have quinoid-type structure.

DISCUSSION

In discussing the nature of these colored substances, the first possibility to be considered is that of an oxidation-reduction reaction in which the nitro compound would oxidize the iodide, probably to furnish iodine. It appears that the color is not due to molecular iodine, however, for several reasons which are recountered here. First, comparison of a solution of the nitro-iodide color with an iodine solution of equal intensity shows that there is a difference in hue. Second, a positive iodine reaction by the starch-iodide test cannot be obtained from one of the nitroaromatic iodide solutions although a genuine iodine solution of equal intensity does give a positive reaction. Third, though the color intensity of the nitroaromatic-iodide solutions is substantially decreased by the addition of relatively small amounts of water, the color intensity of an iodine solution in acetone is not nearly so drastically reduced by the addition of comparable amounts of water. Fourth, the intensity of color of a solution of DNB and sodium iodide in acetone decreases strikingly on dilution with more acetone, whereas a solution of iodine in acetone undergoes only the "normal" expected decrease in intensity when diluted. Fifth, a dilute aqueous solution of sodium thiosulfate does not bleach the color to any greater extent than does an equal volume of water. Lastly, a concentrated acetone solution of the colored material produced by 1,3-dinitrobenzene and sodium iodide (2.0 g. DNB and 3.6 g. of NaI in 20 ml. acetone) was prepared, allowed to stand for 24 hr., and then poured into a large excess of cold water. Of the original 2.0 g. of DNB, 1.78 g. were recovered unchanged. These observations make it seem very unlikely that the reaction is an oxidation-reduction.

The 1:1 combining ratio for both 1,3-dinitrobenzene and for 2,4,6-trinitrotoluene suggests that the combination may be through the aromatic ring rather than through the nitro group(s). The crystal radius of iodide ion (2.2 Å) is nearly the same as that of the aromatic nucleus, making it seem geometrically plausible for the iodide ion to be involved with the aromatic ring as a whole. (This does not explain why 4,4′-dinitrobiphenyl, with two aromatic rings, should also have a 1:1 combining ratio.) Since the nitro group withdraws electrons from the aromatic nucleus, the aromatic nucleus might then attempt to regain electrons by forming some sort of loose complex with the iodide ion. It is worth noting in this connection that the intensity of color increases with increasing numbers of nitro groups in the aromatic ring. The color produced by TNT is deeper than that produced by DNB at the same concentration. It would be interesting to see whether aromatic compounds having substituents with electron-attracting power similar to that of nitro group also give this color reaction.

The color is definitely associated with the iodide ion and not the cation, for potassium iodide and ammonium iodide produce the same effect as sodium iodide. Conductivity data[11] indicate that sodium iodide in acetone at concentrations of $0.1M$ or less is appreciably dissociated into the ions, so it is reasonable to assume that iodide ion is acting as an independent species. The color reaction is not restricted to acetone solutions, for methanol solutions have been observed to give similar results.

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Chemistry Research Branch
Aeronautical Research Laboratory
Wright Air Development Center
Wright-Patterson Air Force Base
Ohio

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Studies in the Pyrazole Series. VII.[1] The Base-Induced Scissions of 3,5-Dimethyl-1-carbamylpyrazole and -1-thiocarbamylpyrazole

F. L. Scott,[2] D. G. O'Donovan, M. R. Kennedy, and J. Reilly

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We have shown previously[3a,b] that 1 guanyl- and 1-nitroguanylpyrazoles, Ia and Ib, respectively, deguanylate under aminolytic conditions with the formation of substituted guanidines and a 1-unsubstituted pyrazole. The corresponding 1-carbamyl- and 1-thiocarbamylpyrazoles, Ic and Id, respectively, have now been shown to behave similarly. Thus the reactions of Ic with amines formed a variety of substituted ureas, as well as 3,5-dimethylpyrazole (II). While the expected thioureas were analogously obtained from the reactions of Id with such bases as aniline, benzylamine, 4,4-diphenylsemicarbazide, hydrazine hydrate, and phenylhydrazine, the corresponding ammonium thiocyanates were isolated from its reactions with cyclohex-

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[2] To whom inquiries concerning reprints are to be sent. Present address, Chemistry Department, University of California, Los Angeles 24, Calif.

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