# A Fatigue Mechanism for Thermochromism in Leucosulfites of Triphenylmethane Compounds

RICHARD N. MACNAIR

*U. S. Army Natick Laboratories, Natick, Massachusetts 01760*

*Received October 23, 1967*

The evidence discussed gives support to the mechanism of fatigue of thermochromism in triphenylmethanes proposed in reaction 4. Since the evidence was obtained on several representative compounds, the mechanism is presumably valid for most triphenylmethanes which show thermochromism in bisulfite solutions. However, it apparently applies only in situations where sulfur dioxide can escape. There is also evidence that one or more mechanisms may be going on concurrently.

Observations of thermochromism in triphenylmethane leucosulfite solutions, made by Dreyer and Harries,[1] indicated that aqueous malachite green solutions fatigued, that is, became nonthermochromic, when heated or irradiated in open vessels. In the process sulfur dioxide was evolved and the nonthermochromic leuco base was formed. The behavior was readily observable with open vessels but not with closed vessels. In a recent review this author proposed[2] that hydrogen may be formed during heating causing reduction of the leucotriphenylmethane to its leuco base and that sulfate ion was also formed. Equations 1 through 3 were suggested for the transformation.

$$\underset{\substack{\text{Malachite green}\\ \text{leucosulfonic acid}\\ \text{I}}}{[p\text{-}(CH_3)_2NC_6H_4]_2C_6H_5CSO_3H} \underset{H_2O}{\overset{\text{heat}}{\rightleftharpoons}} \underset{\substack{\text{Colored species}\\ \text{(undissociated salt form)}}}{[[p\text{-}(CH_3)_2NC_6H_4]_2C_6H_5C]\,{}^{+}HSO_3{}^{-}} \quad (1)$$

$$NaSO_3H + H_2O \overset{\text{heat}}{\rightleftharpoons} NaSO_4H + H_2 \quad (2)$$

$$\underset{\substack{\text{Colored species}\\ \text{(carbonium ion form)}}}{[p\text{-}(CH_3)_2NC_6H_4]_2C_6H_5C\,{}^{+}HSO_3{}^{-}} + H_2 \underset{H_2O}{\overset{\text{heat}}{\rightleftharpoons}} \underset{\text{Leuco base}}{[p\text{-}(CH_3)_2NC_6H_4]_2C_6H_5CH} + SO_2\uparrow + H_2O \quad (3)$$

This sequence implied unintentionally that gaseous hydrogen only is involved in the reduction of the triphenylmethane compound but the evidence indicated that the hydrogen is probably in a much more reactive form. Thus, reaction 4 is perhaps a better summation of the equations.

$$[p\text{-}(CH_3)_2NC_6H_4]_2C_6H_5C\,{}^{+}HSO_3{}^{-} + NaHSO_3 \underset{\text{heat}}{\overset{H_2O}{\rightleftharpoons}} [p\text{-}(CH_3)_2NC_6H_4]_2C_6H_5CH + NaHSO_4 + SO_2 \quad (4)$$

This proposal is supported by several pieces of convincing evidence. First, reaction 2 has been discussed by Diserens[3] who implied that the equilibrium in this reaction is normally far to the left but stated that, if a reducible substance is present, the equilibrium shifts to the right. Thus, bisulfate ion is formed. The reduction of malachite green must take place either in a concerted manner or by a reactive form of hydrogen rather than by gaseous hydrogen since the formation of insoluble hydrogen gas would itself shift the equilibrium. Evidence against the formation of gaseous hydrogen was obtained when several attempts to increase the yield of leuco base by addition of hydrogen gas to the fatigue reaction mixture failed.

Second, the fact that malachite green is easily reduced under mild conditions is well documented. For example, Mauzerall and Westheimer[4] reported the reduction of malachite green to its leuco base with 1-benzyldihydronicotinamide at room temperature.

Third, experiments have confirmed sulfate and leuco base formation in, and sulfur dioxide evolution from, partially or completely fatigued thermochromic solutions. These experiments were carried out with aqueous bisulfite-containing solutions of malachite green (I), brilliant green (II), crystal violet (III), new fuchsin (IV), and pararosaniline (V) shown as leucosulfonic acids.

$[p\text{-}(C_2H_5)_2NC_6H_4]_2r_2C_6H_5CSO_3H$ II

$[p\text{-}(CH_3)_2NC_6H_4]_3CSO_3H$ III

$[p\text{-}H_2N,\ m\text{-}CH_3C_6H_3]_3CSO_3H$ IV

$[p\text{-}H_2NC_6H_4]_3CSO_3H$ V

The sulfate ion and sulfur dioxide formed during heating were determined in partially fatigued solutions. The former was precipitated with barium chloride[5] while the latter was detected satisfactorily in a simple apparatus basically like that of Heisig and Lerner.[6] The observation of these products indicated a definite shift of equilibrium either in reactions 2 and 3 or reaction 4.

The leuco bases of the representative compounds II and III were isolated from completely fatigued thermochromic solutions. Characterization of these compounds was accomplished by spectral methods and was supported by elemental analysis. An increase in the amount of bisulfite used in the fatigue reaction seemed to increase the yield of leuco base at least in the fatigue of crystal violet.

The spectra of the leuco bases were substantially different from the spectra of the starting materials and very similar to the spectra of the model compound, triphenylmethane, indicating a definite change in structure had occurred. The nmr showed the expected bands for the reduced compounds, particularly the singlet C–H bands of the central carbon atoms. These appeared at 5.22 (crystal violet product) and 5.34 ppm

(1) J. F. Dreyer and R. W. Harries, Polacoat, Inc., Blue Ash, Ohio Final Report, Contract DA-19-129-AMC-112(N), U. S. Army Natick Laboratories, Natick, Mass., Feb 1968.

(2) R. N. Macnair, *Photochem. Photobiol.*, **6**, 779 (1967).

(3) L. Diserens, "The Chemical Technology of Dyeing and Printing," Vol. 1, translated and revised from the second German edition by P. Wengraf and H. P. Baumann, Reinhold Publishing Corporation, New York, N. Y., 1948, p 34

(4) D. Mauzerall and F. H. Westheimer, *J. Amer. Chem. Soc.*, **77**, 2261 (1955).

(5) T. R. Hogness and W. C. Johnson, "Qualitative Analysis and Chemical Equilibrium," 4th ed, Henry Holt and Co., New York, N. Y., 1954, p 517.

(6) G. B. Heisig and A. Lerner, *Ind. Eng. Chem., Anal. Ed.*, **13**, 843 (1941).

(brilliant green product) whereas the triphenylmethane singlet C–H band appeared at 5.54 ppm. Tetramethylsilane was used as the standard. The shift in the leuco base bands from that of triphenylmethane is undoubtedly due to the substitution on the phenyl rings. Crystal violet has one more dialkyl amino group than brilliant green and its central carbon C–H band is shifted more than the brilliant green band. The integrated intensities ratios of all the bands observed in the nmr spectra of the products were identical with the theoretical hydrogen atom ratios.

The ultraviolet spectrum of the representative brilliant green product showed broad bands around 218 and 273 mμ, resembling the broad absorption of triphenylmethane around 217 and 264 mμ. In sharp contrast, the starting material absorbed at 230 and 320 mμ. In addition, the visible spectrum of brilliant green had broad bands at 430 and 646 mμ whereas the reduction product was colorless. Similarly, the crystal violet reduction product was colorless.

Since sulfur dioxide and sulfate ion were detected during the thermochromic fatigue of all five compounds studied, we expected that all the leuco bases could be isolated also. However, attempts to isolate the leuco bases of new fuchsin and pararosaniline failed in spite of the fact that the solutions were completely fatigued. Therefore, other fatigue mechanisms including side reactions yielding different organic compounds such as amine oxidation products were indicated. This indication was supported by the fact that the yields of brilliant green and crystal violet leuco bases were relatively low.

Other decomposition or reduction products have been reported in the literature. Conant and Bigelow[7] found that the dimer of malachite green, that is, 1,2-diphenyl-1,1,2,2-tetrakis(*p*-dimethylaminophenyl)ethane, formed when malachite green was reduced with vanadous chloride. The dimer, either dry or wet, decomposed to a black tar and formaldehyde in the presence of air and became a black tar in solution in the presence of oxygen. Desai and Vaidya[8] isolated benzophenones analogous to *p,p'*-diethylamino- and *p,p'*-dimethylaminobenzophenone among the thermal and/or photochemical decomposition products of several triphenylmethane compounds. Also, Henriquez[9] observed dealkylation products. Our crude reduction products of brilliant green and crystal violet both showed a carbonyl band which was absent in the starting materials and which was close to the carbonyl absorption region of the above benzophenones. In addition, the brilliant green product was a black oil. Further isolation and identification of these materials is in progress.

## Conclusion

The evidence obtained not only supports the proposed mechanism for thermochromic fatigue but also helps to explain the photochromic fatigue observed in aqueous bisulfite solutions in open vessels. For example, if a light-attenuating system containing triphenylmethane leucosulfite solutions were exposed to heat during storage or use and sulfur dioxide escaped, then the leuco base could be formed. The effect could be a diminished photochromic as well as thermochromic response because the leuco base is nonphotochromic as well as nonthermochromic.

(7) J. B. Conant and N. M. Bigelow, *J. Amer. Chem. Soc.*, **53**, 676 (1931).
(8) C. M. Desai and B. K. Vaidya, *J. Indian Chem. Soc.*, **31**, 261 (1954).
(9) P. C. Henriquez, *Rec. Trav. Chim. Pays-Bas*, **52**, 991 (1933).

## Experimental Section

In these experiments, approximate $10^{-4}$ *M* aqueous solutions of the triphenylmethane compounds were used. The purity of the compounds was the highest obtainable commercially, that is, certified biological stain grade. They were used without further purification. Decolorization of the solutions was accomplished with just enough bisulfite (9 mg) for each 10-ml aliquot of solution.

The spectra were recorded, respectively, on a Perkin-Elmer 202 ultraviolet-visible spectrophotometer and a Varian A-60 nuclear magnetic resonance spectrometer. The ultraviolet-visible spectra (methanol) were compared to all the available Sadtler standard spectra of the compounds discussed and were found nearly identical with them as expected. The nmr data are given below.

**Detection of $SO_2$.**—The apparatus consisted of a common test tube (150 mm) fitted with a one-hole stopper and having a straight, unconstricted glass tube (7–8 mm diameter) reaching to about 40 mm from the bottom. A restricted-flow tube, such as that used by Heisig and Lerner,[6] did not appear necessary for this determination because more than trace amounts of sulfur dioxide were expected and the escape of a minute quantity was not considered serious.

The glass tube insert was dipped in a reagent solution described below, thus wetting both inner and outer surfaces. The outer surface was wiped clean. About 3 ml of decolorized solution to be tested was placed in the bottom of the test tube and the tube was warmed in a water bath at 70–80°, while being careful not to splash liquid against the inner glass tube. As the $SO_2$ evolved the reagent changed character, either to Turnbulls blue (reagent 1) or to brown or colorless (reagent 2).

This occurred in 1–2 min whether or not a triphenylmethane compound was present.

**Reagent 1** was ferric ferricyanide (freshly prepared). One part of 0.17 *M* potassium ferricyanide $K_3Fe(CN)_6$, one part of 0.3 *M* ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$, and one part of 5 *N* hydrochloric acid were mixed to give a pale greenish or brownish yellow solution.

**Reagent 2** was potassium permanganate prepared by diluting one part of 0.1 *N* potassium permanganate with one part water and one part of 0.1 *N* sodium hydroxide.

**Detection of Sulfate.**—A 20-ml aliquot of leucotriphenylmethane solution was split into two equal parts. One part was heated on a steam bath, while the other remained at room temperature as a control, for 1 to 1.25 hours. At the same time another control solution, identical with the above except without the triphenylmethane compound, was divided and treated similarly. The heating of the solutions was discontinued after an equivalent amount of time. The sulfate was detected by the following method (see Hogness and Johnson[5]) for sulfate in the presence of sulfite. To each solution were added two drops of 6 *N* hydrochloric acid and 1 ml of 0.1 *N* barium chloride. The precipitates were centrifuged; the supernatant liquid was decanted; the precipitates were washed with 5 ml distilled water and recentrifuged; the washings were decanted, and the precipitates were dried in an oven at 100°. The weights of barium sulfate from the heated leucotriphenylmethane solutions ranged from 6.5 to 9.1 mg whereas the barium sulfate from the controls weighed 1.7 to 2.7 mg, respectively. The net yield was thus 4.8 to 6.4 mg of barium sulfate. The sulfate in the controls was a contaminant of the sodium bisulfite used since all three controls yielded the same weight of barium sulfate.

**Detection of the Leuco Bases.**—The triphenylmethane compound (1 mmol) was refluxed well beyond the complete fatigue point of thermochromism with a large excess of sodium bisulfite. The solution was cooled and the crude leuco base was isolated by extraction with ether, drying the ether over sodium sulfate, and evaporating the ether to dryness under reduced pressure. The crude product was purified (see Mauzerall and Westheimer[4]) by extraction with a small portion of 0.2 *M* hydrochloric acid. The acid-insoluble portion of the product, if any, was separated by centrifugation. The aqueous acid layer containing the soluble portion was cooled to 0° in a salt–ice bath and the pH was adjusted to 7.0 with 0.2 *N* sodium hydroxide. The precipitated material

was separated from the aqueous layer by centrifugation (brilliant green product) or extraction with ether (crystal violet product). When ether was used, the extractions were combined and dried over sodium carbonate. Attempts to crystallize the products from aqueous ethanol either failed or were impractical because the products weighed so little. The products were prone to reoxidation during work-up procedures. Specific details for individual compounds are given below.

**Brilliant green** (1 mmol, 421 mg based on the chloride) was refluxed for 21 days and nights with 100 mmol (10.4 g) of sodium bisulfite ($NaHSO_3$). The crude product was a black oil. The purified product was a viscous and colorless oil which tended to turn green and weighed 140 mg (36% yield).

The nmr spectrum ($d_6$-acetone) exhibited a singlet at 7.25 (aromatic C–H), a quartet at 6.83 (*para*-substituted aromatic C–H), a singlet at 5.34 (triphenylmethane C–H), a quartet at 3.36 (aliphatic $CH_2$), and a triplet at 1.12 ppm (C–$CH_3$). The integrated intensity ratio of these bands was 5:8:1:8:12.

**Crystal violet** (1 mmol, 408 mg based on the chloride) was refluxed with 300 mmol (31.22 g) of sodium bisulfite for 4 days and nights. The crude product (white needles, solutions of which turned blue) weighed 31 mg (8.3%).

The nmr spectrum ($d_6$-acetone) showed a quartet at 6.81 (*para*-substituted aromatic C–H), a singlet at 5.22 (triphenylmethane C–H), and a singlet at 2.86 ppm (N–$CH_3$). The integrated intensity ratio for these bands was 12:1:18.

**The effect of bisulfite concentration** on the yield of leuco base was investigated in another experiment. Crystal violet (1 mmol, 408 mg) was refluxed 14 days and nights with 100 mmol (10.4 g) of sodium bisulfite. The fatigued solution was worked up as described to yield 7 mg (1.8%) of white needles similar with those above. The yield, as well as the bisulfite concentration, was thus lower than in the previous experiment.

**The effect of hydrogen gas** on the yield of leuco base was also investigated. Crystal violet (1 mmol, 408 mg) was dissolved with 100 mmol (10.4 g) of sodium bisulfite in 300 ml of water and placed in a Parr hydrogenation vessel. The bottle was charged with 10 lb of hydrogen gas using the normal procedure and shaken for 8 hr at room temperature. No leuco base product could be isolated by the usual isolation procedure.

Another solution identical with the first was prepared and heated at about 50° under 10–15 lb of hydrogen gas pressure in the Parr hydrogenator for 5 days and nights. When cooled and extracted with ether the mixture yielded only 5 mg of impure residue which turned blue indicating that leuco base was present.

Two other solutions were prepared similarly and refluxed in open vessels for about 3 days and nights with hydrogen gas passing through the solutions. The yields of crude product isolated in these experiments was 10 and 12 mg, not significantly higher than the 7-mg yield obtained without the added hydrogen.

**Registry No.**—I, 16097-04-4; II, 16097-05-5; III, 16097-06-6; IV, 16097-07-7; V, 16097-08-8.

# The Correlation of the Electronic Spectra and Acidity of 5-Substituted 2-Nitroanilines with Structure[1]

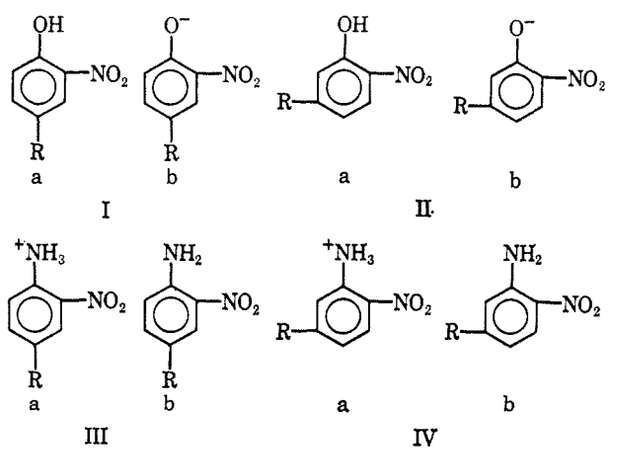
C. KINNEY HANCOCK,[2] ROBERT A. BROWN, AND JOHN P. IDOUX

*Department of Chemistry, Texas A & M University, College Station, Texas 77843*

*Received March 13, 1967*

The electronic spectra and p$K_a$'s of a series of 5-substituted 2-nitroanilines (IV) have been measured. An excellent correlation exists between the resulting p$K_a$'s and Hammett's $\sigma_m$. Structure–spectra correlations for this series are compared with corresponding correlations for 4-substituted 2-nitroanilines (III), 4-substituted 2-nitrophenols (I), and 5-substituted 2-nitrophenols (II). Good correlations exist between the absorption frequencies of I and those of the isoelectronic III, and between the absorption frequencies of II and those of the isoelectronic IV.

Excellent acidity–structure correlations have been reported previously for thirteen 4-substituted 2-nitrophenols[3] (I), eleven 5-substituted 2-nitrophenols[4] (II), and twelve 4-substituted 2-nitroanilines[5] (III). On the other hand, there is very little uniformity in electronic spectra–structure correlations for these three series of compounds.




The structural relationship between the 5-substituted 2-nitroanilines (IV) and III is the same as that between II and I. In view of this fact and of the different spectra–structure correlations found for II[4] compared to those for I,[3] it appeared to be of interest to measure and correlate the electronic spectra and acidities of IV and to compare the results with those found[5] for III.

## Results and Discussion

The electronic spectra and p$K_a$'s of a series of six 5-substituted 2-nitroanilines (IV) have been measured and the results are shown in Table I.

For IVa in aqueous solution, there is an excellent correlation[6a] between the p$K_a$'s and Hammett's $\sigma_m$ constants[7] as shown by eq 1 and Figure 1. For eq 1,

$$pK_a = -0.296 - 3.10\,\sigma_m \quad \underset{-0.999}{r} \quad \underset{0.051}{s} \quad 100.0\% \qquad (1)$$

(1) Abstracted in part from the results of undergraduate research of R. A. B.

(2) To whom inquiries should be sent.

(3) M. Rapoport, C. K. Hancock, and E. A. Meyers, *J. Amer. Chem. Soc.*, **83**, 3489 (1961).

(4) C. K. Hancock and A. D. H. Clague, *ibid.*, **86**, 4942 (1964).

(5) J. O. Schreck, C. K. Hancock, and R. M. Hedges, *J. Org. Chem.*, **30**, 3504 (1965).

(6) G. W. Snedecor, "Statistical Methods," 5th ed, The Iowa State College Press, Ames, Iowa, 1956: (a) Chapter 6; (b) pp 46, 418, and 441; (c) Chapter 14.

(7) H. H. Jaffé, *Chem. Rev.*, **53**, 222 (1953).