COLOUR IN RELATION TO CHEMICAL CONSTITUTION OF THE ORGANIC AND INORGANIC SALTS OF ISONITROSO-PYRAZOLONES AND ISOOXAZOLONES

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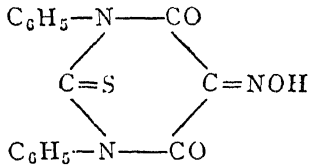
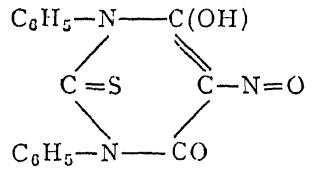
In a previous communication by the present authors,[1] it has been shown that isonitrosodiphenyl-thiobarbituric acid or diphenylthio-violuric acid, which is an orange coloured crystalline compound with the following constitution (I) :



(I) Diphenylthio-violuric acid (Oximino-ketonic form)

forms intensely coloured blue or green salts with alkalies or organic bases, the transition of colour from orange to blue or green being sufficiently strong and sharp for the substance to act as an excellent indicator. The change of colour by the action of alkalies or organic bases has been shown from theoretical considerations to be due to structural change from the above oximino-ketonic (I) to a nitroso-enolic structure (II) given below :



(II) Diphenylthio-violuric acid (Nitroso-enolic form)

This form is more acidic than the oximino-ketonic form, and consequently can produce better salts by complete neutralisation with alkalies and organic bases. And once the nitroso-enolic form becomes stabilised by salt formation, it cannot revert back into the oximino-ketonic form by a process of tautomerisation involving the transference of a hydrogen atom. The nitroso-enolic form in which the constitution of the molecule becomes fixed by salt formation, contains a highly strained nitroso-(N = O) group

which, according to a "Theory of colour on the basis of molecular strain" advanced by Dutt,[2] is the most highly absorptive of all organic groupings, and is consequently the most fruitful cause of intense colour amongst comparatively simple organic compounds. And this has been shown to be the cause of intense colour of organic and inorganic salts of violuric acid by Ghatak and Dutt,[3] of violantin and alloxantin by Gaind and Dutt,[4] of thiovioluric acid by Lal and Dutt[5] and of diphenyl-violuric acid by Prakash and Dutt,[6] the slight differences in the absorption spectra of these various classes of substances being due to differences in the character and molecular weight of groups or radicals attached to the main nucleus of malonyl-urea contained in all of them.

In the present investigation, the problem has been attacked from a different point of view, particularly in relation to substances which do not contain the above-mentioned nucleus in their molecular structure. The compounds that have been taken for the investigation are isonitroso-3-methyl-isooxazolone (III) and isonitroso-3-phenyl-isooxazolone (IV) which have been found to react with alkalies and organic bases with formation of crimson and violet salts respectively, although the free acids are practically colourless, and dissolve in organic solvents to colourless solutions. In these cases also there is not the slightest doubt that the tremendous change of colour brought about by salt formation with alkalies and organic bases must be due to fundamental changes in the constitution of the molecules from oxinimo-ketonic (III and IV) to nitroso-enolic (V and VI) forms as shown in the following diagrams :

Isonitroso-isooxazolones

Oximino-ketonic forms — Nitroso-enolic forms

(III) R = Me : Isonitroso-3-methylisooxazolone (V) Do.

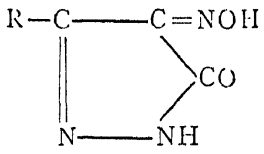
(IV) R = Ph : Isonitroso-3-phenylisooxazolone (VI) Do.

Both isonitroso-3-methyl-, and isonitroso-3-phenyl-isooxazolones dissolve in water and the concentrated aqueous solutions are almost colourless, or at best have only a pale cream coloration like the solids themselves. But on large dilution, a pale pink colour is developed in both the cases which is very characteristic of these substances, and they are in this respect quite analogous to violuric acid which also exhibits such a phenomenon. From this it is also quite apparent that isonitroso-3-methyl, and isonitroso-3-phenyl-isooxazolones must have configurations which are tautomeric

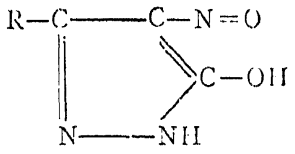
between (III) and (V) and also (IV) and (VI) respectively, according to existing circumstances, and the same argument with regard to their colour phenomena can be adduced as have been given in the cases of diphenylthio-violuric acid and its higher homologues and analogues.

After working with the salts of the isonitroso-oxazolones mentioned above, it was thought advisable to test the accuracy of the above hypothesis, from a different angle of view. If the intense colour of these compounds on salt formation with alkalies and organic bases be really due to the development of a true nitroso-(N = O) group in their molecular structure as the result of the transference of a labile hydrogen atom and production of a more acidic configuration, certainly the colour development will be much less, when there is a possibility of the formation of the same or more acidic configuration, but without the formation of the highly strained nitroso-group. And such a state of things becomes apparent when we take into consideration the salts of isonitroso-3-methyl-pyrazolone (VII) and isonitroso-3-phenyl-pyrazolone (VIII) :

Isonitroso-pyrazolones

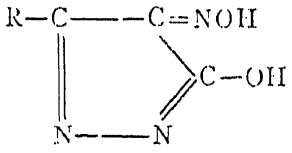


Oximino-ketonic forms



(IX) Nitroso-enolic forms

(VII) R = Me : Isonitroso-3-methyl-pyrazolone
(VIII) R = Ph : Isonitroso-3-phenyl-pyrazolone



(X) Oximino-enolic forms

The above weakly acidic oximino-ketonic structures of 3-substituted isonitroso-pyrazolones may undergo tautomerisation by transference of a hydrogen atom into two more highly acidic enolic forms in accordance with the scheme given above. It can be easily realised that when the comparatively much less strained and more acidic *oximino-enolic* form (X) is capable of existence, the highly strained and less acidic *nitroso-enolic* form (IX) will not be produced, and the colour of these compounds on salt formation will be much less intense than can be expected from a nitroso-enolic structure. From actual experimental evidence we find that the isonitroso-pyrazolones although so closely analogous to the corresponding isonitroso-isooxazolones in structure, yet from the point of view of colour, they are

much weaker, for, whereas the salts of isonitroso-isooxazolones are purple or deep magenta in colour with absorption maxima situated in the neighbourhood of 5800 Å, the salts of the corresponding isonitroso-pyrazolones are orange in shade with the absorption maxima in the neighbourhood of 4800 Å. It is perfectly apparent that the above theoretical exposition of the colour phenomenon of the salts of isonitroso-isooxazolones and isonitroso-pyrazolones is correct and this lends a further additional proof of the correctness of the "Theory of colour on the basis of molecular strain" advanced by Dutt.

The following ten salts of each of the four isonitroso-compounds mentioned above have been prepared and their absorption spectra determined in solution of aqueous acetone: potassium, sodium, ammonium, methylamine, ethylamine, dimethylamine, diethylamine, trimethylamine, *n*-butylamine and piperidine. All these salts are soluble in water with partial dissociation into constituents. In aqueous acetone (acetone containing about 5% of water) however such dissociation does not take place, and the colour of the salt is fully developed. In dry acetone as well as in other organic solvents, the colour is somewhat less intense, and the full intensity is only developed when a small quantity of water is added to the solution in those cases where the water is miscible with the solvents. The isonitroso-pyrazolones and isonitroso-isooxazolones possess remarkable power of crystallisation, and the same property is found transmitted in the salts also.

Experimental

Preparation of isonitroso-3-phenylisooxazolone.—

The method given in literature for the preparation of this compound (Claisen and Zedel[7]) being found to be very unsatisfactory both from the point of view of yield and purity, the following method was devised which gave a satisfactory yield of the pure material. The procedure adopted consists of two stags:—

(1) *Preparation of 3-phenyl-isooxazolone.*—Benzoyl-acetic ester (23 gm.) dissolved in glacial acetic acid (30 c.c.) was treated with hydroxylamine hydrochloride (8 gm.), and the mixture heated under reflux on the wire-gauze until the hydroxylamine hydrochloride completely dissolved and the product assumed a reddish brown colour. The excess of acetic acid was distilled off, and the residue (30 c.c.) allowed to cool, when it solidified completely to a mass of orange yellow crystals. These were washed with alcohol and recrystallised from boiling water, when the product was obtained in the form of pale cream coloured prismatic needles melting at 174° C. The yield was 18 gm.

(4) *Preparation of isonitroso-3-phenyl-isooxazolone.*—A mixture of 3-phenyl-isooxazolone (18 gm.) and sodium nitrite (10 gm.) dissolved in the minimum quantity of aqueous caustic soda (5%) was gradually treated with dilute sulphuric acid while being cooled under the tap, until the light buff-coloured precipitate of the isonitroso derivative was no longer formed. After standing overnight, the product was filtered off, washed with water, and recrystallised from boilling water in pale cream-coloured glistening rhombic prisms melting at 130° C. instead of 120° C. as found by previous workers (*cf.* Claisen and Zedel[7]). The yield was 18 gm.

The substance is soluble in all organic solvents and also in water to colourless or pale cream-coloured solutions. The aqueous, alcoholic or acetone solutions on dilution with water assume a pale pink coloration, thus recalling the behaviour of violuric acid. The substance is very souble in alkalies or organic bases with intense violet colorations.

Preparation of isonitroso-3-methylisooxazolone.—

The original method of preparation of this substance described in literature (Ceresole and Kockert[8] and also Nussberger[9]) being found to be very unsatisfactory due to an impure substance in a microscopic yield, the following new method was devised after a number of unsuccessful trials, which gave an excellent yield of the pure material. The procedure adopted consists of two stages, namely :

(1) *Preparation of isonitroso-acetoacetic ester.*—A mixture of finely powdered sodium nitrite (60 gm.) and acetoacetic ester (100 c.c.) was treated with dilute sulphuric acid (20%) with constant shaking and cooling with cold water, until a slight excess was added and there was no further effervescence. The mixture was allowed to stand overnight and the heavy layer of isonitroso-acetoacetic ester that had separated out was removed and dehydrated with calcium chloride. The yield was practically quantitative. The crude ester was directly converted into the next stage without any further purification.

(2) *Isonitroso-3-methyl-isooxazolone.*—A mixture of isonitroso-acetoacetic ester (120 gm.) and hydroxylamine hydrochloride (60 gm.) together with glacial acetic acid (30 c.c.) was heated on the water-bath until the hydroxylamine hydrochloride completely dissolved and there was no further evolution of hydrogen chloride (1½ hours). The product was diluted with water (30 c.c.) and repeatedly extracted with ether, until the last ethereal extract did not give any crimson coloration with dilute ammonia. The ethereal solution was washed with a little water, dried with calcium chloride and

the ether removed by distillation, when the isonitroso-compound was obtained in the form of a dark-red oil which quickly solidified to a mass of light brown crystals. The product was washed with benzene and recrystallised from pure ether with the addition of a little animal charcoal, when colourless feathery needles melting at 150° C. were obtained. The yield was 46 gm. The substance has got properties very similar to the corresponding phenyl derivative described before.

Preparation of isonitroso-3-phenyl-pyrazolone (Modified Method).—

(1) 3-*Phenyl-pyrazolone.*—This was obtained in good yield by treating benzoyl-acetic ester (28 gm.) with hydrazine hydrate (7 gm.) and alcohol (20 c.c.) and heating the mixture under reflux on a water-bath for ½ hour, when the pyrazolone crystallised out in fine colourless needles melting at 235° C. The yield was almost quantitative.

(2) The pyrazolone obtained above (20 gm.) was ground up with water (200 c.c.) to a fine paste or emulsion, and nitrous anhydride generated from sodium nitrite and dilute sulphuric acid was passed in until the whole mass was saturated and the substance turned orange yellow. The product was filtered off and recrystallised from boiling water in fine glistening orange hexagonal prisms melting at 188° C. Yield was almost quantitative (22 gm. *Cf.* Rothenburg[10]).

Preparation of isonitroso-3-methyl-pyrazolone.—

This was obtained by a modification of the original method described in literature by Curtius,[11] according to the scheme given above in the case of the corresponding phenyl compound, the essential difference between the two being that instead of benzoyl-acetic ester, acetoacetic ester was used. The substance crystallises from boiling water in bright yellow glistening hexagonal prisms melting at 217° C. instead of 130° C. as given by Curtius. The yield obtained was about 85% of the theoretical.

Preparation of salts.—

The isonitroso-pyrazolones and -oxazolones described above were converted into salts by treating the substances dissolved in acetone with a slight excess of the organic and inorganic bases, when in most instances the salt crystallised out from the solution almost immediately in fine glistening crystals. Where however such crystallisation did not occur, the acetone solution of the salt was quickly evaporated at the ordinary temperature with the help of a blast from an electric table fan, when the salt invariably came out in fine form. After washing with ether in order to remove the excess of the base, the product was obtained perfectly pure.

The salts prepared in this way are beautifully crystalline compounds the description and properties of which have been given in tabular forms at the end of the paper. All these susbstances are very soluble in alcohol, acetone and water, moderately soluble in chloroform and insoluble in ether, benzene and petroleum ether. The absorption maxima of these compounds have been determined in aqueous acetone solution with the help of a Hilger constant deviation glass spectrograph, the results being incorporated in the tables mentioned above.

Summary and Conclusions

(1) Like violuric acid and diphenyl-violuric acid, isonitroso-3-methyl-isooxazolone and isonitroso-3-phenyl-isooxazolone have been found to form very intense, *i.e.*, purple and magenta coloured salts with organic and inorganic bases, while the substances themselves are almost colourless and dissolve in water and organic solvents to colourless solutions.

(2) This behaviour of the above-mentioned compounds on salt formation has been shown to be due to a fundamental change in the constitution of the molecules from oximino-ketonic to nitroso-enolic forms with consequent changes in the molecular strain and therefore the absorption of these substances.

(3) The change of colour of these substances from colourless to purple or magenta is sufficiently sharp and intense for them to act as excellent indicators.

(4) The validity of the hypothesis with regard to the colour phenomena of the above-mentioned isonitroso-iso-oxazolones is borne out by taking into consideration the organic and inorganic salts of isonitroso-3-methyl-pyrazolone and isonitroso-3-phenyl-pyrazolone. In these substances there is an alternative more acidic but less strained oximino-enolic configuration possible of existence, and consequently the salts of these isonitroso-pyrazolones have less strained structures and their colours also are far less intense than the corresponding salts of the isonitroso-isooxazolones mentioned before, in spite of all of them possessing very closely analogous molecular structures. The behaviour of all these substances therefore lends a further additional proof to the correctness of the " Theory of colour on the basis of molecular strain " advanced by Dutt.

TABLE I. *Salts of isonitroso-3-phenyl-isooxazolone*

Salt with	Colour in solid state	Remarks	M.P. (Decom.) °C.	Colour in solution	Absorption maxima (Å)	Analysis % N. (Theoretical within bracket)
Methylamine ..	Orange	Glistening rectangular plates	122	Violet	5790	19·20 (19·00)
Ethylamine ..	Deep pink	Glistening rhombic plates	112	Do.	5750	18·20 (17·8)
Dimethylamine ..	Orange-red	Do.	102	Do.	5750	18·10 (17·8)
Diethylamine ..	Do.	Glistening cubical crystals	103	Do.	5690	17·50 (17·0)
Trimethylamine	Yellow	Rectangular prisms	110	Do.	5600	18·20 (18·0)
n-Butylamine ..	Red	Glistening rhombic plates	82	Do.	5730	17·30 (17·0)
Piperidine ..	Crimson	Do.	121	Do.	5620	14·60 (15·2)
Sodium ..	Deep pink	Glistening rectangular prisms	110	Do.	5850	13·60 (13·2)
Potassium ..	Yellow	Glistening needles	122	Bluish-violet	5910	12·07 (12·2)
Ammonium ..	Mauve	Rectangular prisms	86	Violet	5810	19·90 (20·3)
Free acid	Pale cream	Rhombic prisms with silky lustre	130	Pale pink	5300	14·84 (14·7)

TABLE II. *Salts of isonitroso-3-methyl-isooxazolone*

Salt with	Colour in solid state	Remarks	M.P. (Decom.) °C.	Colour in solution	Absorption maxima (Å)	Analysis % N. (Theoretical within bracket)
Methylamine ..	Chocolate-brown	Rectangular plates	107	Deep magenta	5760	26·4 (26·4)
Ethylamine ..	Biscuit	Rectangular prisms	108	Do.	5555	24·7 (24·2)
Dimethylamine ..	Orange	Rectangular plates	102	Do.	5485	24·6 (24·2)
Diethylamine ..	Brownish-orange	Glistening rhombic plates	87	Do.	5430	21·3 (20·8)
Trimethylamine	Orange-brown	Rectangular plates	72	Do.	5350	22·8 (22·4)
n-Butylamine ..	Cream	Cubical crystals	112	Do.	5370	21·4 (20·8)
Piperidine ..	Orange	Rectangular plates	..	Do.	5335	20·1 (19·7)
Sodium ..	Creamy yellow	Rectangular prisms	210	Deep carmine	5860	19·0 (18·6)
Potassium ..	Brownish-yellow	Prismatic needles and plates	..	Do.	5890	16·9 (16·8)
Ammonium ..	Salmon	Rhombic plates	96	Deep magneta	5770	29·4 (28·9)
Free acid ..	Pale cream	Glistening feathery needles	150	Pale pink	5300	21·9 (21·8)

TABLE III. *Salts of isonitroso-3-phenyl-pyrazolone*

Salt with	Colour in solid state	Remarks	M.P. (Decom.) °C.	Colour in solution	Absorption maxima (Å)	Analysis % N. (Theoretical within bracket)
Methylamine ..	Brownish red	Glistening rectangular plates	155	Yellow-brown	4928	25·6 (25·4)
Ethylamine ..	Do.	Do.	170	Orange	4900	24·4 (23·9)
Dimethylamine ..	Orange-yellow	Glistening rhombic plates	185	Orange-brown	4850	23·4 (23·9)
Diethylamine ..	Do.	Do.	193	Brown-yellow	4865	21·8 (21·3)
Trimethylamine	Do.	Do.	185	Do.	4935	22·1 (22·5)
n-Butylamine ..	Do.	Do.	176	Do.	4815	21·2 (21·3)
Piperidine ..	Do.	Do.	211	Do.	4715	20·8 (20·4)
Sodium ..	Brownish-orange	Do.	..	Reddish-brown	4950	19·9 (19·7)
Potassium ..	Orange-brown	Do.	239	Do.	5045	17·3 (17·0)
Ammonium ..	Brick-red	Glistening rhombic prisms	184	Do.	4995	26·8 (27·1)
Free acid ..	Orange	Glistening rectangular and rhombic prisms	188	Orange	4650	22·4 (22·2)

TABLE IV. *Salts of isonitroso-3-methyl-pyrazolone*

Salt with	Colour in solid state	Remarks	M.P. (Decom.) °C.	Colour in solution	Absorption maxima (Å)	Analysis % N. (Theoretical within bracket)
Methylamine ..	Chocolate-brown	Cubical crystals	167	Orange-red	4932	35·7 (35·4)
Ethylamine ..	Reddish-brown	Glistening rectangular plates	135	Do.	4780	32·9 (32·5)
Dimethylamine ..	Brownish-yellow	Rectangular prisms	161	Do.	4770	32·7 (32·5)
Diethylamine ..	Orange-red	Cubical crystals	173	Do.	4770	28·4 (28·0)
Trimethylamine	Brownish-yellow	Rectangular prisms	169	Do.	4755	30·5 (30·1)
n-Butylamine ..	Carmine-red	Glistening rectangular prisms	134	Do.	4770	28·5 (28·0)
Piperidine ..	Orange-yellow	Rhombic plates	158	Do.	4750	26·8 (26·4)
Sodium ..	Turmeric-yellow	Prismatic needles	..	Brownish-red	5080	28·4 (28·18)
Potassium ..	Deep salmon	Rectangular plates	273	Crimson	5180	25·7 (25·4)
Ammonium ..	Orange-yellow	Glistening rectangular prisms	214	Orange-red	4810	39·2 (38·88)
Free acid ..	Yellow	Glistening hexagonal prisms	217	Yellow	4470	33·4 (33·0)

REFERENCES

1. Dharam Dass and Dutt — *Proc. Ind. Acad. Sci.*, 1938, **8**, 145.
2. Dutt .. .. — *J. Chem. Soc.*, 1926, **129**, 1171; *J. Ind. Chem. Soc.*, 1927, **4**, 99.
3. Ghatak and Dutt .. — *J. Ind. Chem. Soc.*, 1928, **5**, 665.
4. Gaind and Dutt .. — *Bl. Acad. Sci. U.P.*, 1933, **3**, 79.
5. Lal and Dutt .. — *Proc. Nat. Inst. Sci. India*, 1937, **3**, 377.
6. Prakash and Dutt .. — *Proc. Nat. Acad. Sci. India*, 1938, **8**, 29.
7. Claisen and Zedel .. — *Ber.*, 1893, **24**, 141.
8. Ceresole and Kockert .. — *Ibid.*, 1881, **17**, 823.
9. Nussberger .. — *Ibid.*, 1892, **25**, 2157.
10. Rothenburg .. — *J. Pr. Chem.*, 1895, **50**, (2), 986, 228.
11. Curtius .. .. — *Ibid.*, 1895, **50**, (2), 512.

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