OPEN ACCESS

Scholars International Journal of Chemistry and Material Sciences
Abbreviated Key Title: Sch Int J Chem Mater Sci
ISSN 2616-8669 (Print) |ISSN 2617-6556 (Online)
Scholars Middle East Publishers, Dubai, United Arab Emirates
Journal homepage: http://saudijournals.com

Original Research Article

A Kinetic Study Based on Spectrophotometric and Titrimetric Evaluation for the Formation of Rubazoic Acid Type Derivative from 4-Amino-1(4-Sulphophenyl) 3-Methyl-2-Pyrazolin-5-One during Its Diazotization

Hafiz Tassawar Hussain[1], Ghulam Shabir[2], Aamer Saeed[2], Noor Hassan[3*], Tayyaba Shabir[4], Zobia Yaseen[5], Saira Irshad[1], Muhammad Nadeem Akhtar[6], Nasir Abbas[1], Shakeel Ahmad[7]

[1]Department of Chemistry, Govt. College University, Faisalabad 38000, Pakistan
[2]Department of Chemistry, Quaid-I-Azam University, Islamabad 45320, Pakistan
[3]School of Chemistry and Chemical Engineering, Beijing Institute of Technology100081, P. R. China
[4]Department of Chemistry, Women University Multan 66000 Pakistan
[5]Department of Chemistry, University of Agriculture Faisalabad 38000 Pakistan
[6]Department of Chemistry, Ghazi University, Dera Ghazi Khan 32200 Pakistan
[7]Institute of Chemical Sciences, Bahauddin Zakariya University, 60800 Multan, Pakistan

DOI: 10.36348/sijcms.2021.v04i07.001 | **Received:** 26.06.2021 | **Accepted:** 29.07.2021 | **Published:** 08.08.2021

***Corresponding author:** Noor Hassan

Abstract

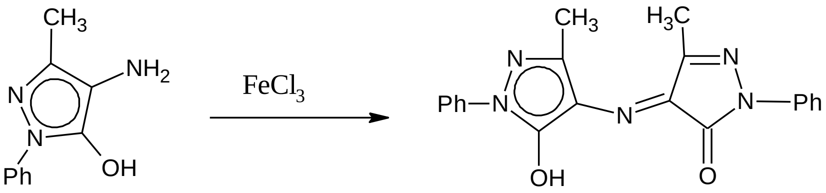
A kinetic study based on spectrophotometric and titrimetric techniques has been carried out for the formation of Rubazoic acid type derivative from 4-amino-1(4-sulphophenyl) 3-methyl-2-pyrazolin-5-one (4-amino SPMP). Physico-chemical factors like effect of Time, pH, aeration and temperature on the formation of Rubazoic acid derivative have been studied in detail. The oxidizing and diazotizing property of nitrous acid has been evaluated for 4-amino-SPMP. Moreover the diazonium compound of SPMP was isolated and its stability in solid form has also been investigated.

Keywords: Rubazioc acid, Sulphophenyl-methyl pyrazolone (SPMP), Nitrosation, Reduction, Diazotization, Coupling etc.

1. INTRODUCTION

Rubazoic acid (I) is chemically (4E)-4-[(5-hydroxy-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)imino]-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (I). Rubazoic acid derivatives have been the subject of extended synthetic study due to their characteristic property of enolic 1,5-diketones in which the OH participates in a strong hydrogen bond [1]. Observed O-O distances are in the range 2.42-2.45 A^o, comparable to the shortest values measured in 1,3-diketones (around 2.4 A^o). The special structure generated by the eight-membered H-chelated ring also shows a favorable O-H-O angle for strong hydrogen bonding which is near 180°. This H-bonding interactions make rubazoic acids derivatives as interesting compounds to probe the nature of the proton potential energy profile both in the liquid and solid states. Many of the water-soluble azo dyes are known to be degraded by intestinal microorganisms in vitro [2] and in vivo [3-5] and rubazoic acid formation occured as intermediate during degradation of dyes. Its formation was first of all reported by Knorr in 1887. It was obtained from 4-amino-1-phenyl-3-methyl-2-pyrazolin-5-one using $FeCl_3$ as an oxidizing agent shown as below.

Citation: Hafiz Tassawar Hussain *et al* (2021). A Kinetic Study Based on Spectrophotometric and Titrimetric Evaluation for the Formation of Rubazoic Acid Type Derivative from 4-Amino-1(4-Sulphophenyl) 3-Methyl-2-Pyrazolin-5-One during Its Diazotization. *Sch Int J Chem Mater Sci, 4*(7): 174-179.



I

Curtius also synthesized Rubazoic acid using ferric chloride method. Later on Ruthenberg also reported the formation of Rubazoic acid as a by-product during the reduction of 4-phenylazo-2-pyrazoline-5-one. Similarly in 1911 Heiduschka and Rothacker also reported its formation during the diazotization of 4-amino-1-phenyl-3-methyl-2-pyrazolin-5-one [6]. Rubazoic acid is valuable compound for the determination of urea, nitrogen and ammonia content in sea water [7-9].

This paper describes a simplified method for synthesis of rubazoic acid from SPMP and effect of pH, Temperature and time on its formation during the reduction of nitroso SPMP to amino SPMP and the diazotization of the respective amine hydrochloride.

2. EXPERIMENTAL

MATERIALS

All the chemicals used were purchased from E. Merck, Sigma-Aldrich and were utilized without further purification. The FTIR spectra were recorded on Agilant Carry 630 FTIR spectrophotometer using diamond ATR. FTIR spectra were taken in absorbance mode at frequency range 4000-650cm^{-1}. UV-visible spectra were measured on Datacolor Spectra-flash SF-550 from 300-700nm.

METHODS

Synthesis of rubazoic acid involves two steps which are as follows:

A-Nitosation of p-Sulphophenyl-3-methyl-5-pyrazolone (SPMP)

SPMP (1) (25.4 g, 0.1 mole) was suspended in H_2O (250 ml). Hydrochloric acid (45 ml) was added to this well stirred suspension. The reaction mixture was cooled to 0-5 °C in an ice bath. A solution of $NaNO_2$ (6.9g, 0.1mol) in H_2O (25 ml) previously cooled to 0 °C, was then added over a period of 35 minutes with stirring. The stirring was continued for an hour maintaining the same temperature, with positive test for nitrous acid. Later on the excess of nitrous acid was destroyed with required amount of sulphamic acid. The Nitroso (Oxime) was filtered after salting out.

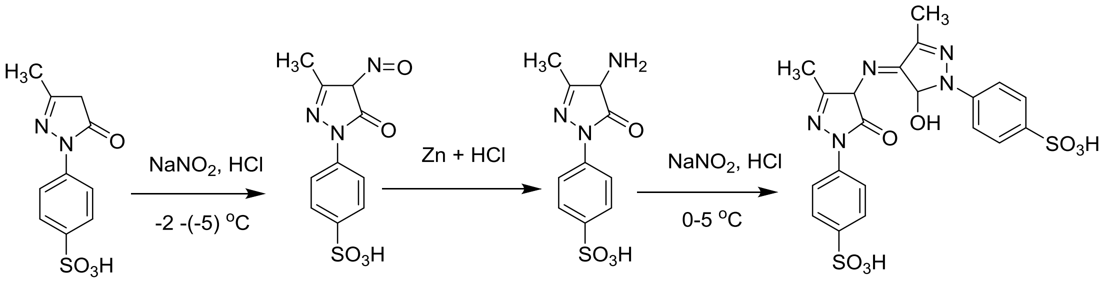
B- Reduction and Diazotization

The nitroso was reduced by stirring in 200ml water containing 85ml HCl and 23g Zinc metal at boil. The amine Hydrochloride formed was diazotized and used for subsequent coupling reactions as described in Result and Discussion.

3. RESULTS AND DISCUSSION

3.1 Effect of temperature on the synthesis of Rubazoic Acid:

Synthesis of rubazoic acid from SPMP was carried out according to the scheme sketched below in scheme 1.



Scheme 1, Synthesis of (*Z*)-4-(4-((5-hydroxy-3-methyl-1-(4-sulfophenyl)-1,5-dihydro-4*H*-pyrazol-4-ylidene)amino)-3-methyl-5-oxo-4,5-dihydro-1*H*-pyrazol-1-yl)benzenesulfonic acid (Rubazoic acid Derivative) from SPMP

1(4-sulphophenyl) 3-methyl-2-pyrazolin-5-one (SPMP) was nitrosated at 0-5°C using $NaNO_2$ and HCl. The nitroso compound was filtered to remove some terry material. The clarified nitroso derivative, that usually exists in an oxime form (as indicated by its FTIR), was salted out by common salt and dried after filtration. Reduction of Nitrso/Oxime of SPMP was carried in two ways. Low temperature reduction of Oxime was carried out at 0-5°C using Zinc and NH_4Cl. The process resulted into the formation of Rubazoic acid of SPMP and its amine as well [10, 11]. High temperature reduction of oxime of SPMP was carried at

100-105ºC using Zinc and HCl. A mixture of water and HCl (3:1) was heated to boiling. The oxime of SPMP and zinc metal were added in small portions at boil. The reduction was completed as the solution became colorless. A small amount of additional zinc was added and the resultant amine hydrochloride was quenched to -7 ºC. The excessive un-reacted zinc was removed by filtration. The comparative results of the both processes for the formation of SPMP amine hydrochloride and Rubazoic acid are presented in Table-1.

Table 1: Reduction of Niroso/Oxime of SPMP

Process	**Oxime (g)**	**Zn used (g)**	**NH4Cl (g)**	**Temp,^{0} C**	**HCl (ml)**	**Aime %age**	**Rubazoic acid%age**
B-1	28.3	7.8	8	3-5	45	85-86	24-25
B-2	28.3	23	0	100-105	85	97-98	2-3

Note: Amine content was determined by Ist Coupling value and Rubazoic acid by Post coupling value.

Table-2: %age of Rubazoic acid formation during diazotization

Sr. No.	**Nitrite addition time (mint.)**	**SPMP amine (moles)**	**Coupler (moles)**	**Coupling pH**	**Coupling Temp(^{0} C)**	**%age of Coupler, Coupled**	**%age of Coupler, Uncoupled**	**Diazotization % age**	**Rubazoic acid % age**
1	1 (At once)	0.1	0.1	8.5-9.5	5-15	zero	100	zero	100
2	3 (Twice)	0.1	0.1	8.5-9.5	5-15	2	98	2	98
3	5 (Thrice)	0.1	0.1	8.5-9.5	5-15	2.5	97.5	2.5	97.5
4	15	0.1	0.1	8.5-9.5	5-15	4.5	95.5	4.5	95.5
5	30	0.1	0.1	8.5-9.5	5-15	10.6	89.4	10.6	89.4
6	45	0.1	0.1	8.5-9.5	5-15	14.3	86.7	14.3	86.7
7	60	0.1	0.1	8.5-9.5	5-15	21.8	78.2	21.8	78.2
8	75	0.1	0.1	8.5-9.5	5-15	30.7	69.3	30.7	69.3
9	90	0.1	0.1	8.5-9.5	5-15	39.3	60.7	39.3	60.7
10	105	0.1	0.1	8.5-9.5	5-15	46.4	53.6	46.4	53.6
11	120	0.1	0.1	8.5-9.5	5-15	53.8	46.2	53.8	46.2
12	135	0.1	0.1	8.5-9.5	5-15	60.1	39.9	60.1	39.9
13	150	0.1	0.1	8.5-9.5	5-15	67.6	32.4	67.6	32.4
14	165	0.1	0.1	8.5-9.5	5-15	81.8	18.2	81.8	18.2
15	180	0.1	0.1	8.5-9.5	5-15	90.9	9.1	90.9	9.1
16	195	0.1	0.1	8.5-9.5	5-15	94.8	5.2	94.8	5.2
17	210	0.1	0.1	8.5-9.5	5-15	97.5	2.5	97.5	2.5
18	225	0.1	0.1	8.5-9.5	5-15	98.3	1.7	98.3	1.7
19	240	0.1	0.1	8.5-9.5	5-15	98	2	98	2
20	255	0.1	0.1	8.5-9.5	5-15	98	2	98	2

3.2 Effect of time on diazotization during synthesis of rubazoic acid:

The amine hydrochloride of SPMP was diazotized using an aqueous solution of $NaNO_2$ (6.9g dissolved in 250ml of solution) and HCl at -5 to -2ºC.The nitrous acid formed in situ can diazotize as well as Oxidize the amine hydrochloride to rubazoic acid. Both of the reactions proceeded competitively. The amount of diazonium formation was quantified by the coupling reaction of β-naphthol. The excess of β-naphthol amount (uncoupled β-naphthol) was determined by its post coupling with a standard p-nitro aniline diazonium chloride solution. H-acid was used as an external indicator in this back titration. The comparative formation of diazonium compound of SPMP and rubazoic acid is given in Table-2. This also shows the rate of nitrite addition, amount of diazotization and the % age of Rubazoic acid formation.

The figure below is the graphic presentation of the data given in Table-2, showing the comparative oxidizing and diazotizing effect of nitrous acid on SPMP amine hydrochloride.

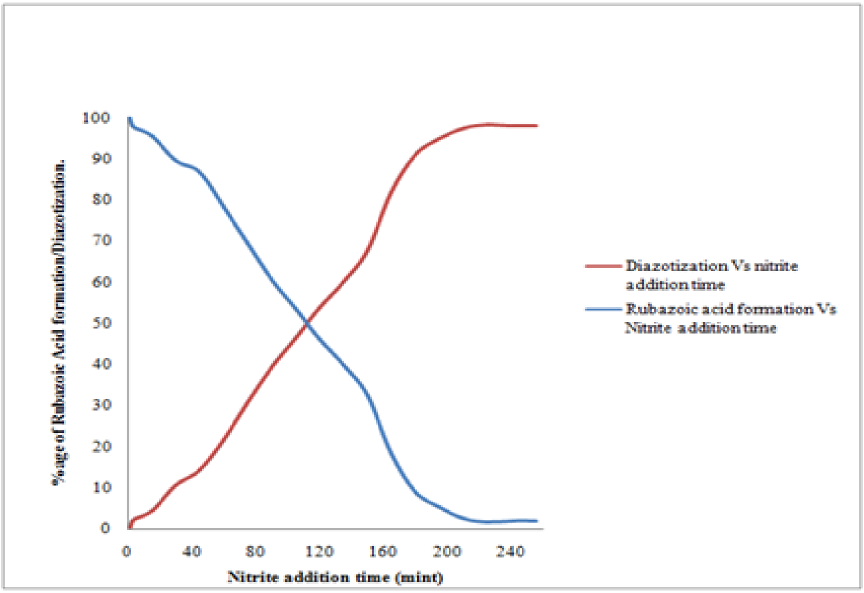


Figure 1, Graphical representation of comparative oxidizing and diazotizing effect of nitrous acid on SPMP amine hydrochloride

The diazonium compound of SPMP formed in step-C was coupled with β-naphthol dissolved in 250 ml water containing 4.5 g NaOH. The solution of coupler was jacketed by ice and coupling was conducted at 5-15^0 C. A 25% solution of Na_2CO_3 was used as an acid binding agent. Coupling was completed in 8-10 hours at pH 8.5-9.5.This coupling value gave us the %age amount of the Diazonium compound of SPMP formed in step-C.

For the determination of uncoupled β-naphthol in step-D, post coupling was done with a standard solution of p-nitroaniline diazonium chloride at 3-5^0 C and 8.0-8.5 pH. The diazonium solution was added from a burette. H-acid was used as an external Indicator. This post coupling value gave us the %age of Oxidation of amine of SPMP (%age of Rubazoic acid formation).

For the synthesis of rubazoic acid of SPMP, the reduction of oxime was conducted as described in step B-1. After the reduction, pH of the amine solution was raised to 5.5 by 10% NaOH. Then aeration was done to oxidize the amine content to form Rubazoic acid.

3.3 Spectral and kinetic Study for formation of Rubazoic acid from SPMP amine

For this purpose amine hydro chloride of Oxime of SPMP was prepared according to method B-2. To 100ml of this solution $Na_2CO_3$was added to precipitate Zinc from this solution as $ZnCO_3$ that was filtered immediately. After the filtration of zinc, 10ml of this solution was diluted up to 500 ml with the requisite phosphate buffer. Now the solution contained amine concentration equivalent to 2.0mMolar.

At pH 7.0 or above SPMP amine is automatically converted into Rubazoic acid and its strength gradually increases as a function of time. To measure the strength of Rubazoic acid, the cell was filled with this solution of amine (2.0mmolar) and the initial reading was taken as standard. The same solution remained in the measuring compartment of the instrument and readings were taken as a function of time till the strength became maximum or constant. This procedure was repeated for every ph variant. The results of Rubazoic acid formation and its strength measurements with respect to pH and Time are presented in Table-3.

Table 3: Spectrophotometric study for the formation of Rubazoic acid and its strength as a function of time from SPMP amine at different pH values

Time(min)	pH=7.0	pH=7.5	pH=8.0	pH=8.5	pH=9.0	pH=9.5	pH=10.0	pH=10.5
0	0	0	0	0	0	0	0	0
5	20.54	30.33	73.76	82.04	105	135.1	360.2	400.39
10	48.51	68.63	122.69	195.46	320.4	386.2	450.65	475.76
15	96.83	138.51	230.52	250.5	430.15	455.63	500	490.1
20	118.25	193.77	340.67	448.9	480.26	490.52	510.23	480.23
25	158.32	215.36	419.74	473.15	495.66	503.26	503.45	456.36
30	198.46	340.84	447.57	486.93	506.08	515.63	495.61	430.48
35	240.15	366.9	453.32	493.97	506.9	516.12	479.35	419.56
40	281.35	398.15	457.32	500.26	510.34	518.96	468.52	405.55
50	319.1	417.4	457.77	508.16	511.95	519.6	460.13	365.12
60	344.64	428.05	459.25	510.45	513035	520.24	459.2	350.4
70	370.36	431.96	460.5	512.3	517.96	521.86	458.56	330.94
80	381.86	432.76	462.68	513.36	520.4	522.9	457.96	322.6
100	406.6	435.5	463.59	515.34	521.23	523.1	456.85	300.54
110	410.4	437.66	465.33	515.96	522	524.2	456.32	298.64
120	412.6	438.9	466.1	516.26	522.6	524.1	456	295.28
150	413.5	439	466.53	516.46	522.7	524	455.65	293.61
180	414.11	439.5	46.83	516.6	522.76	523.86	455.23	292.1
210	415.46	439.52	466.89	516.76	522.78	523.46	455	291.86

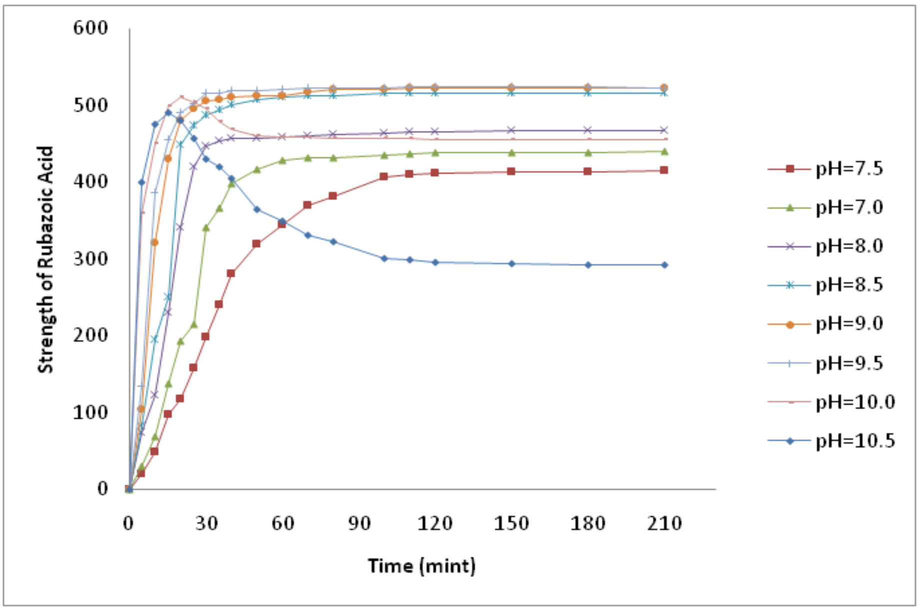


Figure 2, Graphical presentation of Rubazoic acid formation

Synthesis of rubazoic acid from 1(4-sulphophenyl) 3-methyl-2-pyrazolin-5-one (SPMP), involves nitrosation of SPMP, reduction of nitroso derivative and diazotization. During diazotization due to oxidizing action of nitrous acid rubazoic formation occurs which has been confirmed by FTIR of comparision of strating materials, intermediate diazo and and rubazoic acid formed. Broadness peak at range 3200-3500/cm indicated the hydrogen O-H---O=C bonding and the peak at 1556/cm showed the presence of imine functionality formed. Presence of prominent peak at 1715/cm provided the picture of carbonyl group in the molecule. Three peaks at 1635, 1585, and 1570/cm are the evidence for the presence of benze motif in the molecule. Peak at 1220/cm represented the presence of SO_3H group in the rubazoic formed.

4. CONCLUSION

In this work it has been found that rubazoic acid type derivative of SPMP is formed in water automatically at pH 7.0 or above. The amine hydrochloride of SPMP was stable at -7^0 C .The best diazotization temperature for this amine has been found to be -5 to -3^0 C. At a temperature, above this range, amine hydrochloride is oxidized by nitrous acid to form rubazoic acid. Rubazoic acid of SPMP is formed at a greater rate at higher pH as well. Deterioration of rubazoic acid derivative starts above pH 10. The higher rate of nitrite addition formed greater amount of nitrous acid that favored the formation of Rubazoic acid, while a slow addition of nitrite leaded to greater %age of diazotization.

5. ACKNOWLEDGMENTS

We gratefully acknowledge to Shafi Reso Chemicals private Ltd. for providing research facilities at its R&D lab.

REFERENCES

1. Bertolasi, V., Gilli, P., Ferretti, V., Gilli, G., & Vaughan, K. (1999). Interplay between steric and electronic factors in determining the strength of intramolecular resonance-assisted NH··· O hydrogen bond in a series of β-ketoarylhydrazones. New Journal of Chemistry, 23(12), 1261-1267.
2. KING, T., CHUNG, K. T., & GE, F. (1978). REDUCTION OF AZO DYES BY INTESTINAL ANAEROBES.
3. Klitgaard, A., Iversen, A., Andersen, M. R., Larsen, T. O., Frisvad, J. C., & Nielsen, K. F. (2014). Aggressive dereplication using UHPLC–DAD–QTOF: screening extracts for up to 3000 fungal secondary metabolites. Analytical and bioanalytical chemistry, 406(7), 1933-1943.
4. Scheline, R. R., Nygaard, R. T., & Longberg, B. (1970). Enzymatic reduction of the azo dye, acid yellow, by extracts of Streptococcus faecalis isolated from rat intestine. Food and cosmetics toxicology, 8(1), 55-58.
5. Roxon, J. J., Ryan, A. J., & Wright, S. E. (1967). Enzymatic reduction of tartrazine by Proteus vulgaris from rats. Food and cosmetics toxicology, 5, 645-656.
6. Hrbáčke, J., Dvořáková, M., Kořínek, V., & Prochazkova, L. (1961). Demonstration of the effect of the fish stock on the species composition of zooplankton and the intensity of metabolism of the whole plankton association: With 22 figures on 2 Folders. Internationale Vereinigung für theoretische und angewandte Limnologie: Verhandlungen, 14(1), 192-195.
7. McCarthy, J. J. (1970). A Urease Method for Urea in Seawater 1. Limnology and Oceanography, 15(2), 309-313.
8. Duffin, G. F., & Kendall, J. D. (1954). The reaction of diazonium salts with 1-aryl-Δ 2-pyrazolines. Journal of the Chemical Society (Resumed), 408-415.
9. Fasman, G. D. (2019). CRC Handbook of Biochemistry and Molecular Biology: Lipids, Carbohydrates, Steroids. Crc Press.
10. Peltz-Steele, R. (2016). FTAs in Asia-Pacific:“Next Generation” of Social Dimension Provisions on Labor? Ronald Brown Wrongs, Rights, and Remedies: A Yankee Romp in Recent European Tort Law. Law Review, 26(2).
11. Heiduschka, A., & Rothacker, O. (1911). Über das 1- Phenyl- 3- methyl- 5- pyrazolon und Über das 1- Phenyl- 3- methyl- 4- amino- 5- pyrazolon. Journal für Praktische Chemie, 84(1), 533-542.