SPECTRAL DETECTION OF TERMINAL RING QUINONES

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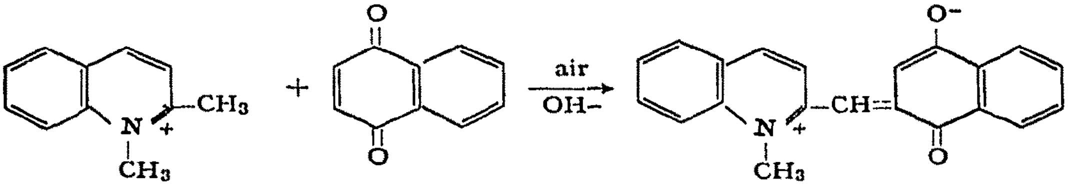
INTRODUCTION

Specific colorimetric methods for the analysis of all types of quinones are in critical need. Terminal ring quinones, such as benzoquinone and α-naphthoquinone, have been detected with ethyl malonate in alkaline solution[1]. KESTING has reported that color tests are given by benzoquinone, α-napthoquinone and β-naphthoquinone in alkaline alcoholic solution on reaction with malononitrile, ethyl benzoylacetate, acetylacetone, or benzoylacetone[2-4]. CRAVEN[5] has obtained brilliant, although unstable, color reactions for benzoquinone, o-toluquinone, chloranil, thymoquinone, and α-naphthoquinone with ethyl cyanoacetate in alcoholic ammonia. β-Naphthoquinone did not react. In dilute alkali, nitromethane is stated to give a blue color with α-naphthoquinone and a violet color with β-naphthoquinone[6]. In our laboratory, many of these reagents were tried in alkaline 2-methoxyethanol solution. In many cases unstable colors and insensitive reactions were obtained. For this reason a group of new reagents for the colorimetric analysis of quinones is introduced in this paper. Quinones giving a positive test contain the grouping $O{=}\overset{|}{C}{-}\overset{|}{C}{=}\overset{|}{C}{-}X$, where X is hydrogen or halogen. The reagents are azonium heterocyclic derivatives containing an activated methyl group *ortho* or *para* to the azonium nitrogen. The mechanism involves addition of the methyl group to the activated double bond of the quinone followed by air oxidation to a blue or green dye, *e.g.* with N-methylquinaldinium iodide and α-naphthoquinone the following reaction takes place:



The dye, I, has been prepared by KIPRIANOV[7] and absorbs at 670 mμ in alcohol.

EXPERIMENTAL

Reagents

Lepidine, quinaldine, 2-methylbenzoxazole, 2-methylbenzothiazole, 1-ethyl-quinaldinium iodide, and 1-ethyl-2,6-dimethylquinolinium iodide were obtained from Distillation Products; 6-ethoxyquinaldine was obtained from the Aldrich Chemical Co.

The azonium methosulfates were prepared by slightly modified procedures of the following preparation of 1-methyl-quinaldinium methosulfate: 28 g of quinaldine and 25 g of methyl sulfate were mixed thoroughly in an ice bath. The mixture was allowed to stand at room temperature until an exothermic reaction had taken place and the mixture had solidified. The product was crystallized from *n*-propyl alcohol. The 6-ethoxy derivative was prepared in a small volume of boiling acetone; the lepidine derivative was prepared at room temperature. Details of these preparations can be found in the literature[8].

Benz [e] acephenanthrylene-9,12-dione, m.p. 248–249°, was prepared by literature procedure[9].

Equipment

A Cary Model 11 Recording spectrophotometer was used for wave-length measurements. For time studies an American Optical Company Rapid Scan Spectrophotometer was used.

Test procedure

To an accurately measured 5–50 ml of the 2-methoxyethanol test solution was added 1 ml of a 2% 2-methoxyethanol solution of the quinolinium reagent. The mixture was shaken, and after 8–9 min it was diluted to approximately 50 ml with 2-methoxyethanol. Ten min after the addition of reagent, 2 ml of 10% aqueous tetraethylammonium hydroxide was added, followed by dilution of the mixture to 100 ml with 2-methoxyethanol. Within ten min the absorption spectrum was determined from 500–800 mμ. The data on the more intense and much more stable long wave-length band are reported in Table I. One-tenth the volumes can also be used in the procedure.

TABLE I

SPECTRAL DETECTION OF TERMINAL RING QUINONES

Compound	λ_{max} (*sens.*)[a]				
	1,2-Dime[b]	*1-Et-2-me*[c]	*1-Et-2,6-dime*[c]	*1,2-Dime-6-etO*[b]	*1,4-Dime*[b]
Benzoquinone	650 (0.007)	655 (0.010)	670 (0.006)	685 (0.006)	700 (0.008)
2,5-Dichlorobenzoquinone	655 (0.012)	685 (0.025)	660 (0.025)	670 (0.014)	715 (0.014)
Chloranil	655 (0.013)	660 (0.020)	660 (0.090)	670 (0.008)	715 (0.023)
1,2-Naphthoquinone	670 (0.060)	670 (0.060)	660 (0.060)	635 (0.060)	720 (0.057)
Sodium 1,2-naphthoquinone -4-sulfonate	660 (0.045)	670 (0.30)	655 (0.045)	640 (0.040)	685 (0.044)
1,4-Naphthoquinone	660 (0.023)	660 (0.023)	675 (0.019)	685 (0.013)	700 (0.020)
2-Methyl-1,4-naphthoquinone	635 (0.043)	675 (0.070)	650 (0.041)	665 (0.027)	670 (0.027)
2,3-Dichloronaphthoquinone	675 (0.15)	675 (0.027)	690 (0.014)	700 (0.012)	720 (0.019)
Benz[e] acephenanthrylene -9,12-dione	715 (0.025)	670 (0.022)	735 (0.020)	750 (0.025)	775 (0.10)

[a] In μmoles per 3 ml giving an optical density of 0.1 in a cell of 1-cm path length.
[b] Quinolinium methosulfate.
[c] Quinolinium iodide.

DISCUSSION

In a previous paper a novel thermochromic test for polynuclear inner-ring *p*-quinones was described[10]. With this test the presence of large polynuclear *p*-quinonic type compounds was demonstrated in air particulates. In the present tests inner-ring *o*- and *p*-quinones, such as phenanthraquinone, 5,6-chrysenequinone anthraquinone, and naphthacenequinone gave negative results. Other types of aromatic carbonyl compounds, such as anthanthrone, benzanthrone, fluorenone, benzophenone, acetophenone, benzalacetone, salicaldehyde, 2-hydroxy-1-naphthaldehyde, and *p*-dimethylaminobenzaldehyde also gave negative results. As far as could be determined the tests described in this paper are specific for terminal-ring quinones.

Many activated methylene compounds were found to give color reactions with terminal ring quinones in alkaline dimethylformamide or 2-methoxyethanol solution, *e.g.* nitromethane, malonitrile, diketene, 3-thenoyl-1,1,1-trifluoroacetone, benzoylacetonitrile, 3-ethylrhodanine, 3-methyl-1-phenyl-5-pyrazolone, ethoxymethylenemalononitrile, and diethyl ethoxymethylenemalonate.

The nonketonic methylene reagents (*e.g.* malononitrile, nitromethane, etc.) gave unstable colors under the conditions of the procedure, while the ketonic methylene reagents apparently reacted with themselves slowly in alkaline solution to give colored dyes. This self-condensation is indicated by a study of the stability of the color obtained in the reaction of 3-ethylrhodanine with chloranil. Visually the color of the solution changed drastically with time while spectrally the 650 mμ band changed but slightly over a period of one-half hour, Fig. 1. The color change from green to dirty brown is due to the reaction of 3-ethylrhodanine, probably with itself, to give a dye absorbing at 530 mμ. This byproduct interferes with the color test but not with the spectral test.

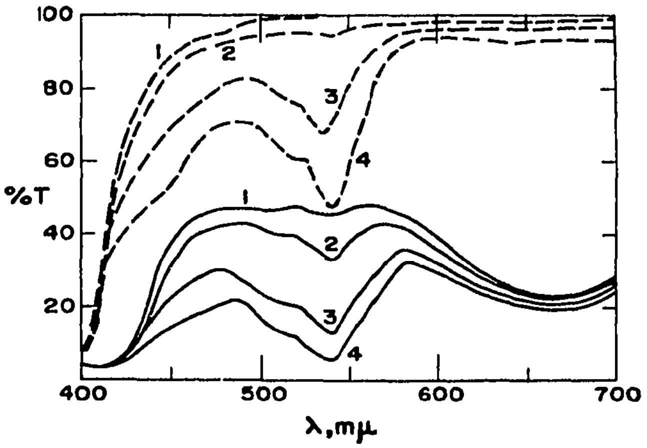


Fig. 1. Effect of time on visible absorption spectra. 10^{-4} *M* chloranil reacted with a 2% solution of 3-ethylrhodanine in 2-methoxyethanol by standard procedure. Blank solutions (minus chloranil) (– – –); Test solutions (———): 1. three min; 2. six min; 3. sixteen min; 4. thirty min, after addition of alkali. All solutions ran against 2-methoxyethanol containing 2% of a 10% aqueous solution of tetraethylammonium hydroxide.

3-Ethylrhodanine appeared to be the best of the activated methylene compounds, *e.g.*, in dimethylformamide solution by the standard procedure – with *p*-benzoquinone, λ_{max} 635 mμ, sens. 0.007; chloranil, λ_{max} 650 mμ, sens. 0.04; 2,3-dichlorobenzoquinone, λ_{max} 660 mμ, sens. 0.01; 1,4-naphthoquinone, λ_{max} 715 mμ, sens. 0.025; 2-methyl-1,4-naphthoquinone, λ_{max} 720 mμ, sens. 0.05; 2,3-dichloro-1,4-naphthoquinone, λ_{max} 705 mμ, sens. 0.05, and benz[e]acephenanthrylene-9,12-dione, $\lambda_{max} >$ 800 mμ. 1,2-Naphthoquinone and its 4-sodium sulfonate derivative gave green colors which faded rapidly. 2-Hydroxy-1,4-naphthoquinone gave negative results with all the reagents.

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Of all the compounds tried as reagents, the quinaldinium derivatives gave the most sensitive and stable colors (green in all instances) (Table I). The wave-length maxima for the dyes formed in the test ranged from 635–775 mμ. In most cases the benzoquinone derivatives gave the most sensitive reaction while the two 1,2-naphthoquinone derivatives gave the least sensitive reaction. If the quinones are analyzed within 10 min after they are reacted with a quinolinium derivative, there is very little change in the color or intensity of the long wave-length band. Over a period of 1–1/2 h, new bands arise near 560 mμ and gradually increase in intensity, eventually interfering with the analysis in the long wave-length region (Fig. 2).

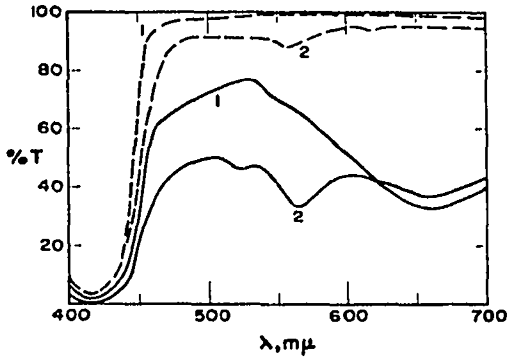

Fig. 2. Effect of time on visible absorption spectra. $2 \cdot 10^{-5}$ *M* chloranil reacted with a 2% solution of 1-ethyl-2,6-dimethylquinolinium iodide in 2-methoxyethanol by standard procedure. Blank solution (minus chloranil) (– – –); Test solutions (———); 1. three min; 2. eighty min, after addition of alkali. All solutions ran against 2-methoxyethanol containing 2% of a 10% aqueous solution of tetraethylammonium hydroxide.

SUMMARY

Terminal ring quinones can be detected specifically by a simple spectroscopic method involving reaction of the quinone with quinaldinium or lepidinium salts in alkaline solution. Other types of quinones and carbonyl derivatives have given negative results. 3-Ethylrhodanine can also be used as a reagent, especially for terminal ring *p*-quinones. All of these colorimetric procedures are amenable to quantitation.

RÉSUMÉ

Un groupe de nouveaux réactifs est proposé pour l'analyse colorimétrique de quinones.

ZUSAMMENFASSUNG

Chinone lassen sich colorimetrisch mit Hilfe von Chinaldin-oder Lepidin-salzen in alkalischem Medium nachweisen.

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