

Spectral Reflectance Studies of Some Nitrophenols and Their Salts on Solid Surfaces

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The behavior of some nitrophenols and their sodium salts adsorbed on lithium, sodium, and potassium carbonates was studied. For each phenol, regular hypsochromic shifts of the wavelength maxima in the visible diffuse reflectance spectra of the two-component system were observed in order of decreasing size of the adsorbent cation whereas for the phenolic salts, essentially the same wavelength maxima were obtained over the three alkaline adsorbents. This phenomenon is interpreted in terms of polarization theory and the concept of "ionization" of the phenols on the surface of the basic adsorbents. A comparison of the reflectance spectra of the phenols and their sodium salts indicates that "ionization" or stretching of the hydrogen-oxygen bond in the phenol is not extensive in case of the three weakly acidic mononitrophenols on the three carbonates and is in the order $\text{Li}_2\text{CO}_3 > \text{Na}_2\text{CO}_3 > \text{K}_2\text{CO}_3$. The more acidic dinitro- and trinitrophenols are believed to exist on the basic adsorbents predominantly in the "ionized" form. Study of the relationship between acidity of the phenols and shift of wavelength maxima in their reflectance spectra on the adsorbents shows an increasing shift with increasing pK of the phenol.

INTRODUCTION

Various investigators have reported the use of spectral reflectance to examine the spectral characteristics of species in the solid state and to study phenomena occurring on the surfaces of solids (1-9). Most recently Zeitlin and co-workers (10, 11) measured the reflectance spectra of the mononitrophenols adsorbed on a series of alkali metal carbonates and alkaline earth oxides. The reflectance wavelength maxima in the visible region were found to increase with decreasing effective nuclear charge of the cation in both series. The relative magnitudes of the shifts, evidenced visually by a change in color in the phenol upon adsorption, was interpreted in terms of electronic polarization theory. A major unresolved question in this work was the nature of the chemisorbed species on the surface of the adsorbent. A plausible interpretation which suggested itself during the

study involved the concept of "ionization" of the phenol in the solid state under the influence of the crystal field of the basic adsorbents, leading to the formation of the phenoxide anion. However, no experimental evidence was advanced to support this view.

The present report is concerned with an extension of the previous work of Zeitlin and co-workers with the mononitrophenols to include various di- and trinitrophenols with the hope of shedding light on the nature of the species adsorbed on the surface of the adsorbent. The approach adopted included (1) the preparation of the sodium salt of the phenols, (2) a study of the behavior of the salts when mixed with lithium, sodium, and potassium carbonates, (3) measurement of the diffuse reflectance spectra of the two-component systems composed of the salt and the alkali carbonate adsorbent and comparison of these spectra

with those of the corresponding phenol-alkali carbonate systems.

EXPERIMENTAL

The phenols used were from the following sources: *o*-nitrophenol, *m*-nitrophenol, 4,6-dinitro-*o*-cresol, 2,4-dinitrophenol from Eastman Organic Chemicals, *p*-nitrophenol from Matheson Coleman and Bell, picric acid from Allied Chemical and Dye Corporation. The melting points of these compounds indicated satisfactory purity. The adsorbents used were "Baker Analysed" reagent grade Li_2CO_3 , Merck reagent grade Na_2CO_3 and K_2CO_3 .

The pK values for all phenols were obtained from the literature (Table 3) with the exception of 4,6-dinitro-*o*-cresol which was calculated from the pH of the dilute aqueous solution.

The salts were prepared by careful neutralization of each phenol with alcoholic or aqueous sodium hydroxide and were purified by repeated recrystallization from anhydrous ethanol. The phenols and salts were ground to a fine powder in an agate mortar and stored over P_2O_5 under anhydrous conditions at room temperature. The adsorbents were similarly ground and sieved through a fine mesh screen. The powders of 100–140-mesh particle size range retained for the study were dried by prolonged heating at 110°C prior to use.

All diffuse reflectance spectra (320–600 $\text{m}\mu$) were recorded with a Beckman DK-2 spectrophotometer equipped with a standard reflectance attachment. The cell used to hold the sample and the reference standard was similar to that employed and described by Frodyma, Frei, and Williams (15). The reference standard consisted in each case of the same pure adsorbent used in the sample cell containing the phenol or phenol salt-adsorbent system.

Since the systems composed of the phenol or phenolic salt adsorbed on carbonate are sensitive to moisture, precautions were taken throughout all manipulation for its exclusion. The two powdered components (*ca.* 2 mg phenol–100 mg adsorbent) were mixed in a glove dry box which had been

dried by dynamic adsorption through activated silica gel for 12 hr. Phosphoric anhydride was placed in the box as an additional drying agent. The mixture was then shaken manually in a sealed tube for several minutes. Immediate interaction occurred as indicated by distinct color changes in the mixture and the spreading and adsorption of the phenol on the surface of the adsorbent. Although all visible phenomena appeared to be at an end after 5 to 10 min., a minimum of 48 hr was allowed to ensure an equilibrium state. In the case of the salts, it was found in preliminary experiments that interaction between phenolic salt and alkali carbonate occurred when the two powdered components were mixed by manual shaking for several minutes or by placing a layer of the salt on top and in direct contact with the carbonate at 110°C . In the first instance interaction was indicated by a distinct color change of the mixture and in the case of the heat treatment a definite color change of the adsorbent was observed in the region adjacent to the phenolic salt within 24 hr. An attempt was made to prepare samples by mixing the two components both at room temperature and by heating. It was found that the reaction rate at room temperature was very slow and equilibrium could not be reached in a period of several weeks, while prolonged heating resulted on occasion in the partial decomposition of the phenolic salt. In light of the above difficulties to induce satisfactory interaction by the mentioned procedures, the method adopted in the preparation of samples containing phenolic salts for spectral measurements consisted of grinding and mixing the two components at repeated 30-sec intervals in a small agate mortar. In this manner, equilibrium was attained in a few minutes.

RESULTS AND DISCUSSION

Figures 1–2 give typical graphs obtained from the solid system measured at equilibrium, in which absorbance is plotted versus wavelength. Tables 1 and 2 contain a compilation of the wavelength maxima

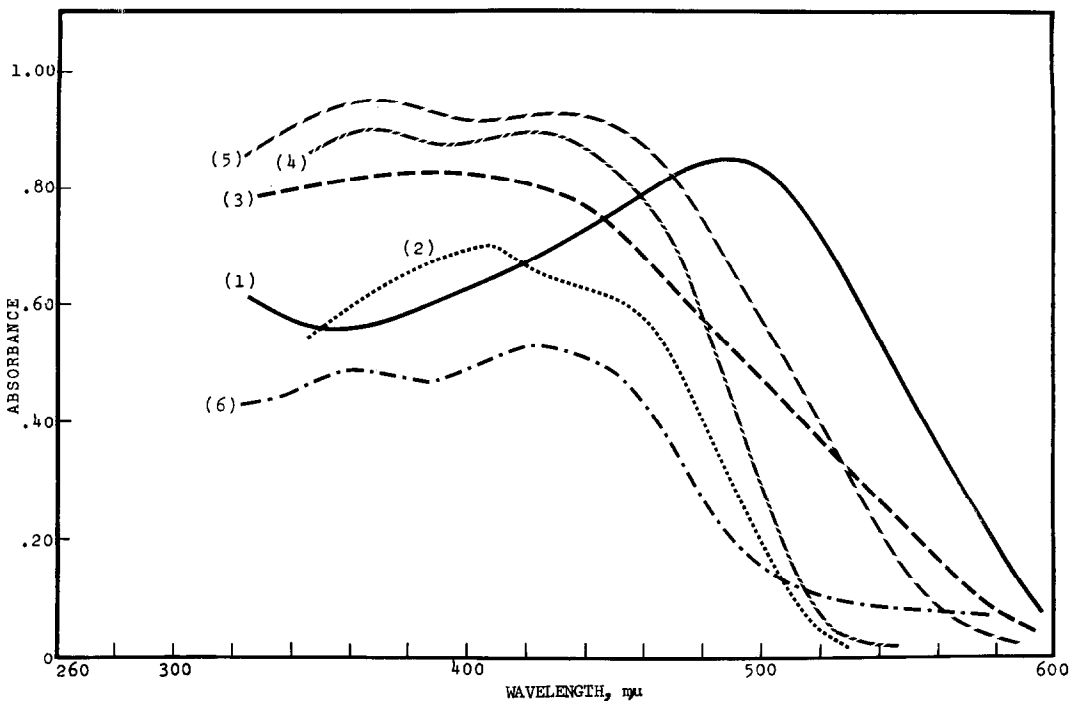


FIG. 1. Reflectance spectra of (1) *o*-nitrophenol, (2) *p*-nitrophenol, (3) *m*-nitrophenol, (4) 2,4-dinitrophenol, (5) 4,6-dinitro-*o*-cresol, (6) 2,4,6-trinitrophenol in equilibrium on solid potassium carbonate.

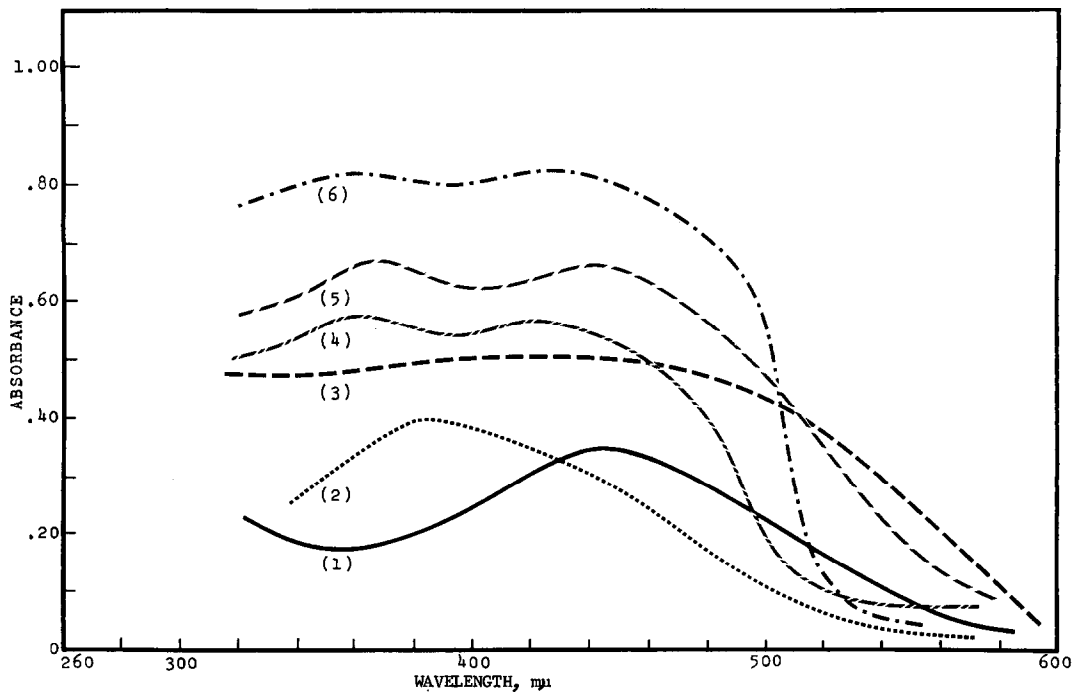


FIG. 2. Reflectance spectra of the sodium salts of (1) *o*-nitrophenol, (2) *p*-nitrophenol, (3) *m*-nitrophenol, (4) 2,4-dinitrophenol, (5) 4,6-dinitro-*o*-cresol, (6) 2,4,6-trinitrophenol in equilibrium on K_2CO_3 .

found in the reflectance spectra of phenols and phenolic sodium salts on alkali carbonates. Although more than one wavelength maximum was present, the peak which underwent regular shifts as a result of change in environment was in the red end and is referred to as the long wavelength absorption peak.

TABLE 1
LONG WAVELENGTH ABSORPTION PEAKS ($m\mu$)
AT EQUILIBRIUM OF VARIOUS PHENOLS AND
THEIR WAVELENGTH SHIFTS OVER THE
THREE ALKALINE CARBONATES

	Li ₂ CO ₃	Na ₂ CO ₃	K ₂ CO ₃	Shift
<i>o</i> -Nitrophenol	425	448	488	63
<i>p</i> -Nitrophenol	325	383	408	83
<i>m</i> -Nitrophenol	331	347	387	56
2,4-Dinitrophenol	408	418	424	16
4,6-Dinitro- <i>o</i> -cresol	424	422	430	6
2,4,6-Trinitrophenol	418	418	421	3

The spectra (Figs. 1, 2) contain broad peaks of the type commonly encountered in reflectance spectra of species in the solid state. Consequently it is difficult to assign precise values to these peaks. The data given in Table 1 represent averages obtained by the measurement and examination of a large number of spectra which

TABLE 2
LONG WAVELENGTH ABSORPTION PEAKS ($m\mu$)
AT EQUILIBRIUM OF VARIOUS PHENOLIC
SODIUM SALTS AND THEIR WAVELENGTH
SHIFTS OVER THE THREE
ALKALINE CARBONATES

Sodium salt	Li ₂ CO ₃	Na ₂ CO ₃	K ₂ CO ₃	Shift
<i>o</i> -Nitrophenol	442	439	441	1
<i>p</i> -Nitrophenol	385	385	385	0
<i>m</i> -Nitrophenol	425	425	425	—
2,4-Dinitrophenol	412	412	418	6
4,6-Dinitro- <i>o</i> -cresol	435	438	440	5
2,4,6-Trinitrophenol	422	420	422	0

are reproducible. The values given are believed to have a precision of ± 2 – $3 m\mu$. Table 3 gives the pK values of the phenols together with their wavelength shifts. The shift refers to the difference in millimicrons between the absorption peaks of the phenols adsorbed on lithium carbonate and

potassium carbonate, the latter serving as the reference.

An examination of the data compiled in Table 1 obtained for each phenol at equilibrium over the three alkaline carbonates shows a hypsochromic shift in each case going from K₂CO₃ → Na₂CO₃ → Li₂CO₃. In contrast, examination of the data in Table 2 shows for all the phenolic salts studied that the wavelength shifts are relatively small and the long wavelength absorption peaks are essentially the same over the three alkaline carbonates. It is

TABLE 3
THE pK VALUES OF VARIOUS NITROPHENOLS
AND THE WAVELENGTH SHIFTS OF THEIR
LONG WAVELENGTH ABSORPTION PEAKS
($m\mu$) AT EQUILIBRIUM OVER THE THREE
ALKALINE CARBONATES

	Shift	pK	Reference
<i>o</i> -Nitrophenol	63	7.23	12
<i>p</i> -Nitrophenol	83	7.14	12
<i>m</i> -Nitrophenol	56	8.35	12
2,4-Dinitrophenol	16	4.11	13
4,6-Dinitro- <i>o</i> -cresol	6	4.42	(See Experimental)
2,4,6-Trinitrophenol	3	0.84	14

noteworthy that in comparing the data in Tables 1 and 2, the adsorption of the free phenol containing a potentially acidic hydrogen atom results in a distinct and regular shift of the long wavelength absorption peak over the three alkali carbonates, whereas the adsorption of the phenol salt consisting of the phenoxide and sodium ions gives rise to no such wavelength shift.

The following interpretation is advanced to account for the phenomena observed. The spreading of the salts on the surface of the basic adsorbents occurred much in the same manner as the free phenols, a phenomenon not believed to have been reported previously. The spectra of the salts are those of the phenoxide anions (and sodium cations) in the adsorbed state with little or negligible differentiating effect on the part of the varying effective nuclear charges of the cations of the carbonates,

thus accounting for the lack of significant spectral shifts on the three adsorbents (Table 2).

The hypsochromic shifts observed with the free phenols on the carbonates were in agreement with previous findings by Zeitlin, Kondo, and Jordan (10). Displacements were interpreted by these workers in terms of polarization theory. The effective nuclear charge of the cation of the adsorbent increases in the order $K^+ < Na^+ < Li^+$. The increased effective nuclear charge of the cation in the crystal lattice results in enhanced polarization, high excitation energy with resultant hypsochromic shifts. In addition, when the free nitrophenols are adsorbed on the basic carbonates, it is believed that the phenols behave in such a fashion which would be equivalent to "ionization" or stretching of the oxygen-hydrogen bond on the solid surfaces. It seems likely that the degree of separation of the hydrogen from the oxygen in the hydroxyl group is dependent upon the extent of stretching between the hydrogen atom and the phenoxide moiety, which in turn is governed by the effective nuclear charge of the alkali metal cation. The evidence indicates that the degree of this separation may be characterized by the wavelength shift of the absorption peak from some reference point such as the absorption peak of the phenol adsorbed on K_2CO_3 (Table 1). This adsorbent contains cations with the smallest effective nuclear charge and the phenol adsorbed on it should, according to the view presented, undergo the smallest degree of "ionization." Consequently, the optical absorption peak of the phenol on K_2CO_3 has been employed as the reference in the calculation of the wavelength shift on the carbonates.

The above argument applied to the three mononitrophenols which are relatively weak acids would suggest that the equilibrium condition is in favor of the unionized phenols in the adsorbed state. The equilibria, however, are influenced to a certain degree by the effective nuclear charge of the cation of the adsorbent. Consequently as this charge increases in the order of $K^+ < Na^+ < Li^+$ the degree of

"ionization" of the phenol should increase in this order. The absorption peaks obtained from the three carbonates are believed to be characteristic of an equilibrium state of both free phenol and its "ionized" form. The free phenolic character should increase in order of decreasing effective nuclear charge of the adsorbent cation and the "ionized" form character increase in the opposite order. As a consequence, the wavelength of the absorption peak of the weak phenol varies, resulting in a regular shift over the three carbonates.

In the case of the di- and trinitrophenols, which are much stronger acids, the equilibrium state on the basic adsorbents would be shifted significantly in favor of the "ionized" form. It is believed that with these acids the phenols are present on all three carbonates predominantly in the "ionized" state and as such, the cations of the adsorbents are not able to exert their normal differentiating nuclear charge. As a result, the wavelength absorption peaks obtained are more characteristic of the phenoxide ion and the proton and not surprisingly do not vary greatly for all three carbonates (Table 1, Fig. 1). This conclusion is also supported by a comparison of the wavelength maxima for the three strong acid phenols (Table 1) and the three corresponding sodium salts (Table 2, Fig. 2) which show striking similarities. The slight differences may be attributed to the presence of the proton in one series as compared to sodium cations in the other.

It has not yet been established whether the "ionization" referred to in this investigation actually involves a separation of the proton from the phenol molecule in the solid state or a stretching of the oxygen-hydrogen bond the extent of which is dependent upon the adsorbent environment. For this reason no distinction is made between the two. However, although the cleavage or stretching of a bond, as the case may be, in the solid state is probably not commonly encountered, it apparently is not an isolated phenomenon, as shown by recent work by Kortum and Vogel (16).

These workers have supplied evidence to the effect that the crystal field of an

active adsorbent is capable of breaking a chemical bond such as that involved in the separation of the proton of the phenol. In a study of the behavior of colorless malachite green-*o*-carbonic acid lactone, which turns blue upon adsorption on a series of alkali halides, these workers have demonstrated that the adsorbents were able to cause a cleavage of the lactone ring in the solid state with the formation of a zwitterion.

Finally, the relation implied between the shifts of the long wavelength absorption peaks and the acidity of the phenols was confirmed by comparing these shifts (Table 1) and their pK values. The data, summarized in Table 3, demonstrate the definite relationship between them. Generally, the shift increases with increasing pK or the weaker the acid the greater is the wavelength shift, which is in accord with the experimental data (Table 3). An analogous correlation for phenols in aqueous solution was recently reported by Rapoport, Hancock, and Meyers (17) in a study of the relation between the wave-number shift caused by the removal in alkaline solution of the phenolic hydrogen in 4-substituted 2-nitrophenols and their pK values.

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