

Infrared Spectra of Some Troponoid and Aromatic Compounds adsorbed on Column Chromatogram

著者	KINUMAKI Susumu, IKEGAMI Yusaku
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	10
page range	315-324
year	1958
URL	http://hdl.handle.net/10097/26883

Infrared Spectra of Some Troponoid and Aromatic Compounds adsorbed on Column Chromatogram*

Susumu KINUMAKI and Yusaku IKEGAMI

The Chemical Research Institute of Non-aqueous Solutions

(Received July 15, 1958)

Synopsis

Some examinations were made on infrared absorption spectra of substances as adsorbed on silica gel or activated alumina in column chromatography. From the results obtained with several troponoid and aromatic compounds, it was found that the spectrum of the adsorbed substance can be obtained by measuring the adsorbent carrying the substance by the potassium bromide disk method when the amount adsorbed is comparatively large. This method will be useful for the identification of organic compounds and studies on the mode of their adsorption. Results obtained from some troponoid and aromatic compounds possessing hydroxyl, amino, or carbonyl as the functional group indicated that there is no drastic change in their spectra when using silica gel. Phenol adsorbed on alumina already showed the spectrum of Ph-O⁻ ion type. The $\nu(\text{C}=\text{O})$ band of adsorbed ketones shifted to a lower frequency region.

I. Introduction

Studies on examination of the state of a molecule adsorbed on a solid surface, using infrared absorption spectrum, have not been numerous to date. This is probably due to the fact that the adsorbent itself had a strong absorption band in the infrared region and also because the adsorbent tended to scatter light that a special technique was necessary for the measurement of infrared spectrum in adsorbed state. The first of such studies in this field was made by Yoroslavskii and others⁽¹⁾ of U. S. S. R. in 1949 who used porous silica in examining variations in harmonics of $\nu(\text{O}-\text{H})$ at around 1.5μ in various aromatic molecules. Several reports have since been published using this porous silica,⁽²⁾ aerosil silica,⁽³⁾ or silica gel.⁽⁴⁾ On the other hand, Eischens and his school have been making detailed studies on the state of molecules adsorbed on the surface of silica-alumina cracking catalyst⁽⁵⁾ or on copper, nickel, palladium, or platinum supported on silica.⁽⁶⁾ More recently, Karagounis and others⁽⁷⁾ discussed the infrared spectra of naphtha-

* Presented in part at the Annual Meeting of the Chemical Society of Japan in Tokyo in April 3, 1958.

- (1) N. G. Yoroslavskii and A. N. Terenin, *Doklady Akad. Nauk. S. S. S. R.*, **66** (1949), 885 (C. A., **43** (1949), 7343).
- (2) For example, A. N. Sidorov, *Doklady Akad. Nauk., S. S. S. R.*, **95** (1954), 1235 (C. A., **49** (1955), 8703); *Zhur. Fiz. Khim.*, **30** (1956), 995 (C. A., **51** (1957), 12656); N. Sheppard and D. J. C. Yates, *Proc. Roy. Soc.*, **A238** (1956), 69.
- (3) For example, R. S. McDonald, *J. Am. Chem. Soc.*, **79** (1957), 850.
- (4) T. Yoshino, *J. Chem. Phys.*, **23** (1955), 1564.
- (5) J. E. Mapes and R. P. Eischens, *J. Phys. Chem.*, **58** (1954), 1059.
- (6) For example, W. A. Pliskin and R. P. Eischens, *J. Chem. Phys.*, **24** (1956), 482.
- (7) G. Karagounis and O. Peter, *Z. Elektrochem.*, **61** (1957), 827.

lene and trichlorobenzene of unimolecular layer prepared on the surface of silica or silver iodide.

The foregoing are all reports on the use of infrared spectra in studying on adsorption or catalyst surface. In the present study, however, adsorption in column chromatography, now being used for separation and purification of organic compounds, has been taken up as a new experiment, and examinations were made to see whether the spectrum of adsorbed molecule would be obtained, *per se*, when organic substances are absorbed on silica gel or activated alumina used for chromatography, and how their spectra changed from those of pure substances.

Before going into experiment, there were still some problems to be solved. One was that the adsorbent itself had absorptions in the infrared region and this limited the usable range to a certain region. The second was the amount to be adsorbed, which was directly related to the polarity of the adsorbed molecule and activity of the adsorbent. Since the present study was to be concerned primarily with column or liquid chromatography, large amount of adsorption could not be expected and it would probably be something like one-tenth the amount of the adsorbent, at the most. The third problem was the granular size of the adsorbent, the smaller the grain, the easier will be the spectral measurement since such grains would be less likely to cause light scattering. As long as these problems remain, it is unavoidable that the spectral measurements are limited to a certain narrow range of substances which could satisfy these problems.

If a part of the adsorbed layer in column chromatography could be cut out and this is used directly for spectral measurement, the process could be utilized for identification of substances in organic chemistry, while it may be expected to offer certain means for the study of adsorption in chromatography.

In the following sections, results obtained on several troponoids* and aromatic compounds will be described.

II. Experimental

(1) *Infrared Measurement.* Infrared absorption spectra were measured with Perkin-Elmer Model 21 infrared spectrophotometer with a NaCl prism. All the solid substances were measured by the KBr disk method.**

(2) *Adsorbents in Chromatography.* Silica gel was a Merck product for chromatography. Grains finer than 180 mesh were collected and dried in vacuum at 200~220°C for ca. 5 hours. Alumina was a Wako Pure Chemicals product "Activated Alumina for Chromatography." Grains of 300 mesh were collected and dried in vacuum at 350~400°C for ca. 8 hours. No further tests were made as to the properties these adsorbents, such as the degree of activity and ability of separation.

* Troponoid is a generic term for tropone, tropolone, and their derivatives.

** The refractive index of activated alumina, measured microscopically, was $n=1.64$. Therefore, KI would be more suitable for measurements in the region of 3000 cm^{-1} , because the refractive index of KI is closer to this than that of KBr.

Fig. 1 is the infrared spectra of these adsorbents for chromatography and these spectra also require further examinations in conjunction with the properties of the adsorbents. However, they provide a comparatively stable background after these adsorption procedures and are considered to be sufficient for the present purpose. The regions of $3200\sim 1300\text{ cm}^{-1}$ and $900\sim 650\text{ cm}^{-1}$ in silica gel, and the region of $3100\sim 1200\text{ cm}^{-1}$ in alumina are available for spectral measurement of the adsorbed substances.

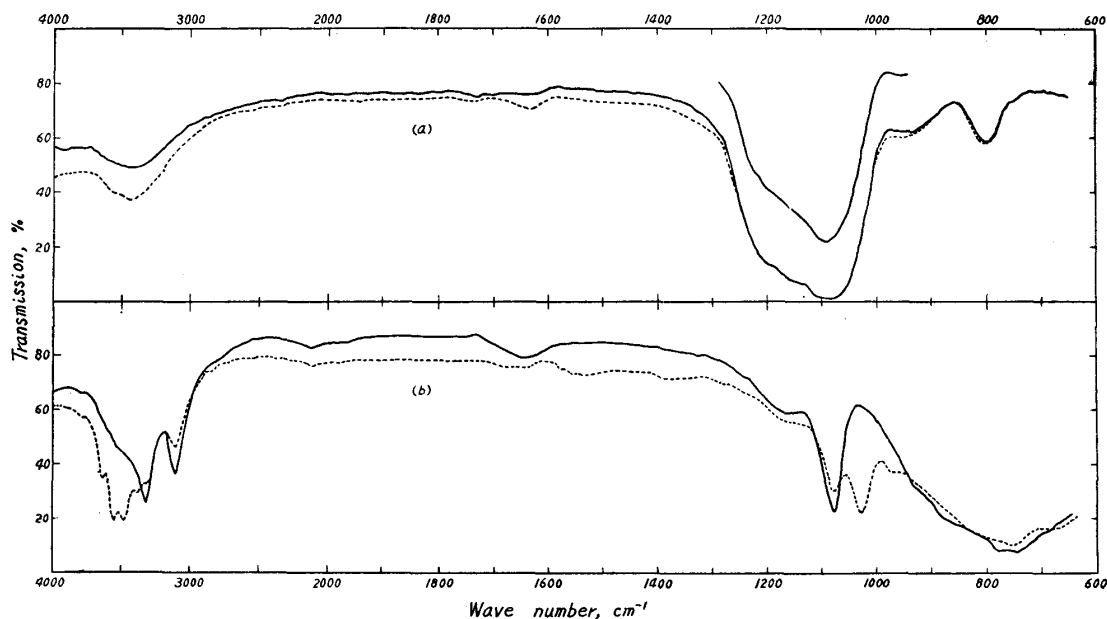


Fig. 1. Infrared spectra of silica gel and activated alumina.

- (a) Silica gel (Merck), fine powder for partition chromatography.
 ... Before drying, — After drying for 5 hrs. at $200\sim 220^{\circ}\text{C}$ in vacuo.
 (b) Activated alumina (Wako), 300 mesh for chromatography.
 ... Before drying, — After drying for 8 hrs. at $350\sim 400^{\circ}\text{C}$ in vacuo.

(3) *Solvent for Adsorption.* The solvent for adsorption in chromatography was petroleum ether (b. p. $66\sim 67^{\circ}\text{C}$) or benzene. Both were washed with conc. sulfuric acid, dried over calcium chloride, distilled, and further dried with metallic sodium. The concentration of the solution during adsorption was below 1 per cent.

(4) *Experiment with *o*-Nitroaniline.* As an example of the spectra to be obtained by actual procedure under the foregoing conditions, experiment with *o*-nitroaniline will be described below.

Silica gel was flown into a glass tube with inside diameter of 0.5 cm. with petroleum ether to make a column of about 7 cm. in height. A solution of 20 mg. of *o*-nitroaniline dissolved in 30 cc. of petroleum ether was poured over this column and the column was developed with 30 cc. of petroleum ether, by which an orange yellow adsorption layer of ca. 1.5 cm. in length formed. The amount of *o*-nitroaniline adsorbed on this column was about 150 mg. to 1 g. of silica gel. The middle portion of this adsorption band was taken out, left in a vacuum desiccator for several hours, and this was submitted to infrared spectral measurement by the KBr disk method. The spectrum thereby obtained is shown in Fig. 2 (b). The same

procedure, using alumina as the adsorbent and benzene as the solvent afforded the spectrum shown in Fig. 2 (c). The column used was a yellow band of about 2.5 cm. in length and the amount of the compound adsorbed was ca. 40 mg. for 1 g. of alumina. The same results were obtained on spectral measurements by the Nujol mulling method.

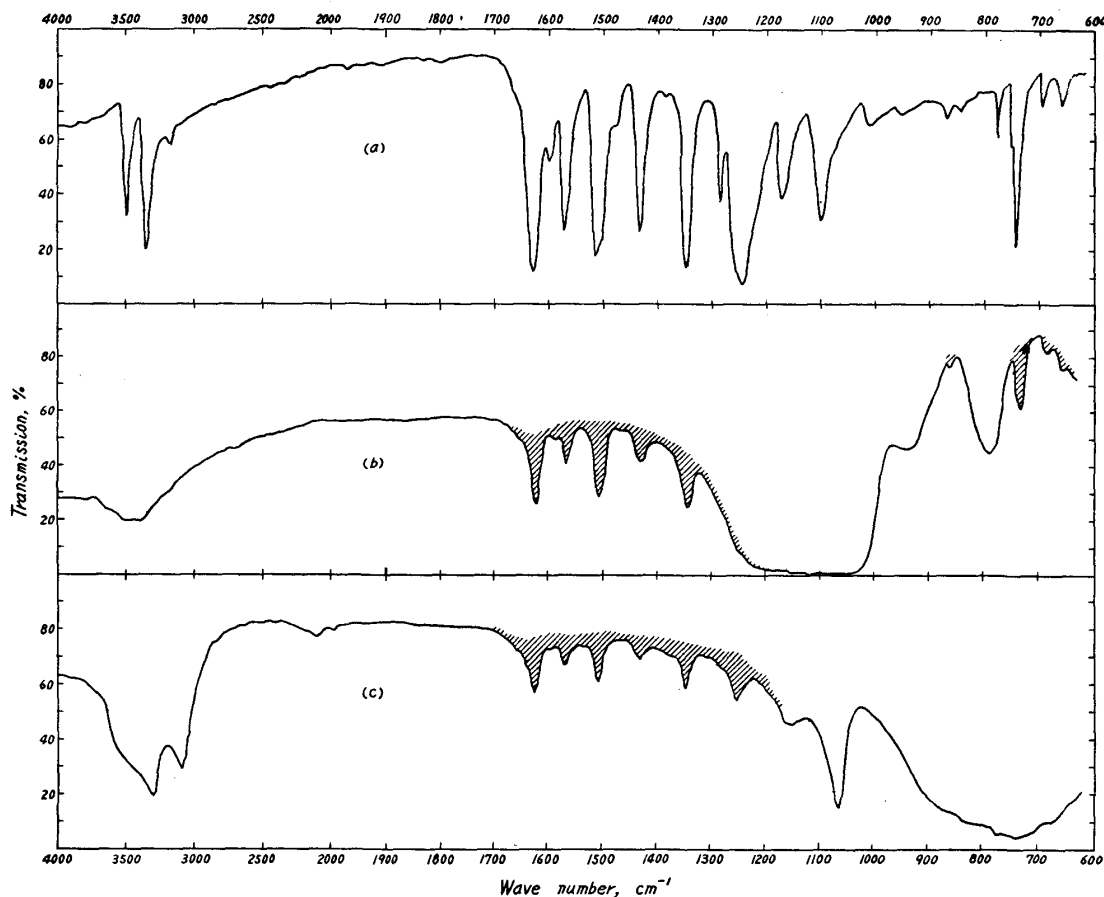


Fig. 2. Infrared spectra of *o*-Nitroaniline.

- (a) Pure crystal
- (b) Adsorbed on silica gel in column chromatography
- (c) Adsorbed on activated alumina in column chromatography

The portions shaded with oblique lines in (b) and (c) in Fig. 2 are the spectral bands of adsorbed *o*-nitroaniline. Compared with that of the pure substance indicated by (a) in Fig. 2, there can be seen no great change in the position of absorption bands and relative intensity. This is one of the examples of the use of this procedure for identification of organic compounds.

III. Results and discussion

Results obtained by spectral measurement of 16 kinds of troponoid and aromatic compounds will be described by classifying them into three classes by their functional groups; the phenolic hydroxyl compounds, amines, and ketones. The position of absorption bands in the region of 1700~1200 cm^{-1} in the spectra obtained is illustrated in Figs. 3, 5, and 6. For the sake of comparison, spectra of each

substance in solid and in solution are also shown.

(1) *Phenolic Hydroxyl Compounds*. The compounds (I) to (VIII) indicated in Fig. 3 all possess phenolic hydroxyl group and a strong hydrogen bond in the molecule, or acid group. Naturally, absorption bands for $\nu(\text{O-H})$ and $\delta(\text{O-H})$ are of interest in these compounds but these absorptions are not clear due to overlapping with that of the adsorbent and to the small amount of the compound adsorbed.

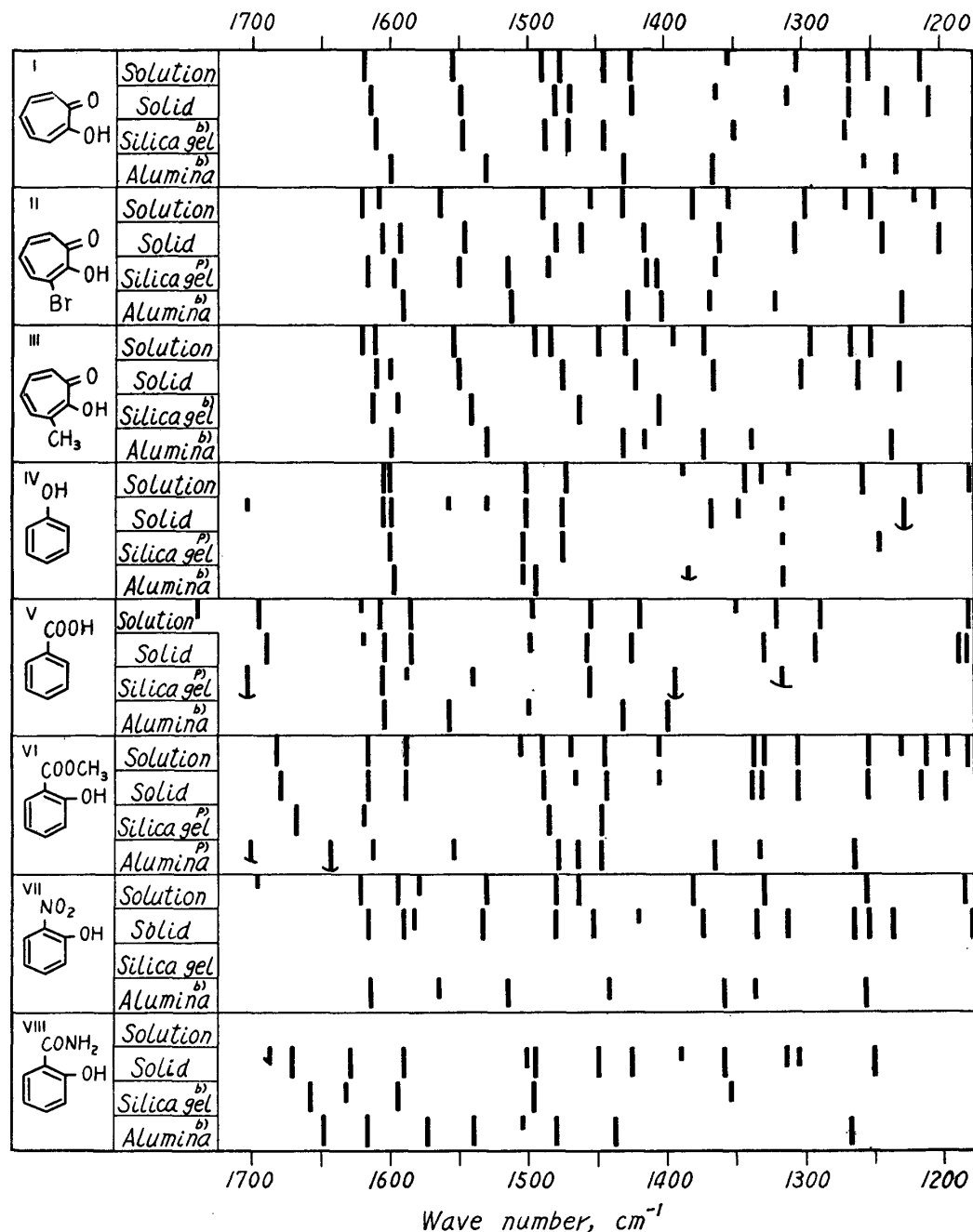


Fig. 3. Position and approximate intensity of absorption bands of phenolic hydroxyl compounds and benzoic acid (1700~1200 cm^{-1} range).

Solution: In carbon tetrachloride (concn. < 4%)

Solid: As KBr disk

Silica gel: Adsorbed on silica gel

Alumina: Adsorbed on activated alumina

b): Adsorbed from benzene solution

p): Adsorbed from petroleum ether solution

The same can be said of the absorption bands for $\nu(\text{C-H})$ and $\nu(\text{N-H})$ of these compounds to be described later.

There seems to be no great difference in the position of absorption bands between those of the three kinds of tropolone adsorbed on silica gel and their pure substances, but there is some shift on comparing each absorption band. For example, the frequency of $\nu(\text{C=O})$ of 3-bromotropolone (II) and 3-methyltropolone (III) on silica gel is closer to that in solution than in the solid, while the C=O band in tropolone (I), on the contrary, appears in a smaller frequency range than that in the solid. However, it would be difficult to argue the state of absorption merely from the whole range illustrated. The same can be said of the compound indicated from (IV) and others and only the band for $\nu(\text{C=O})$ is comparatively clear. In both methyl salicylate (VI) and salicylamide (VIII), the band for $\nu(\text{C=O})$ has shifted about 10 cm^{-1} to a lower frequency region, and these compounds possessing intramolecular hydrogen bonding also show the same tendency as that of ketones described in the following section (3).

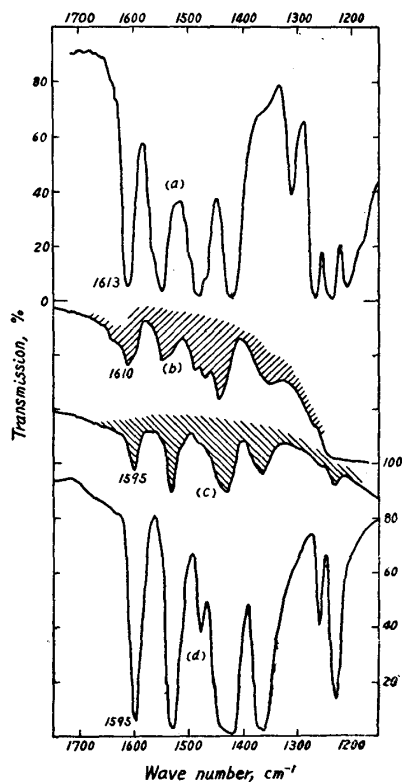


Fig. 4. Infrared spectra of tropolone and aluminum tropolonate (in $1700 \sim 1200\text{ cm}^{-1}$ range) by KBr disk method.

- (a) Tropolone (m.p. 50°)
- (b) Tropolone adsorbed on silica gel
- (c) Tropolone adsorbed on activated alumina
- (d) Aluminum tropolonate (m. p. $>290^\circ\text{C}$)

As for the $\nu(\text{C=O})$ in benzoic acid, the band has shifted to a higher frequency side, nearer that of the monomer than that (1690 cm^{-1}) in the solid, when it is present as a dimer, but is on a lower frequency side than that (1740 cm^{-1}) of the monomer. In the region of 1400 cm^{-1} , the broad band of strong intensity at 1420 cm^{-1} , considered to originate in the vibration of a C-O-H group in the dimer, has shifted to 1393 cm^{-1} by adsorption on silica gel. This seems to suggest that the adsorption is due to a strong interaction between acid and silica rather than in the dimer form. In *o*-nitrophenol with a strong intramolecular hydrogen bond, its spectrum was not obtained due to the small amount adsorbed on silica gel.

In contrast to these spectral results obtained from silica gel chromatography, a fairly different spectra have been obtained from the use of alumina as the adsorbent. It is known as an experimental fact that when phenolic hydroxyl compounds and acids are applied to alumina chromatography, they cannot be eluted out even with solvent with strong power of desorption, such as ethanol, and this is true in the case of tropolone.⁽⁸⁾ From such a point of

(8) In this case, desorption can be effected by elution with ethanol containing a few per cent of hydrochloric acid but alumina is also reacted at the same time and is eluted out as a salt.

view, it may not be quite appropriate to consider this as adsorption but the procedure is sufficient for examining the state of bonding.

Fig. 4 indicates the spectra of tropolone in various states and aluminum tropolonate (m. p. $> 290^\circ$) in the region of 1700 to 1200 cm^{-1} . These spectra show that the spectrum of tropolone adsorbed on alumina is more similar to that of aluminum tropolonate than that of pure tropolone. Since the spectrum of this aluminum tropolonate is generally also found in the metal salts of tropolone,⁽⁹⁾ it can be seen that tropolone is supported in the state, if not completely, nearly that of the ion. The same can be said of 3-bromotropolone (II) and 3-methyltropolone (III).

In the case of phenol and benzoic acid, the strong absorption band at 1227 cm^{-1} (liquid) in phenol, and absorptions corresponding to the COOH group at around 1690 cm^{-1} and at 1300 cm^{-1} in benzoic acid have disappeared from their adsorbed spectra on alumina. In the latter, there are new bands at 1557 and 1399 cm^{-1} corresponding to $-\text{COO}^-$ ion.⁽¹⁰⁾ These facts signify that these compounds are adsorbed in the form of $\text{C}_6\text{H}_5-\text{O}^-$ and $\text{C}_6\text{H}_5-\text{COO}^-$ ions, respectively. Similar tendency may be seen in the compounds (VI), (VII), and (VIII) in Fig. 3, and the fact indicates that alumina behaves completely like a base against series of these kinds

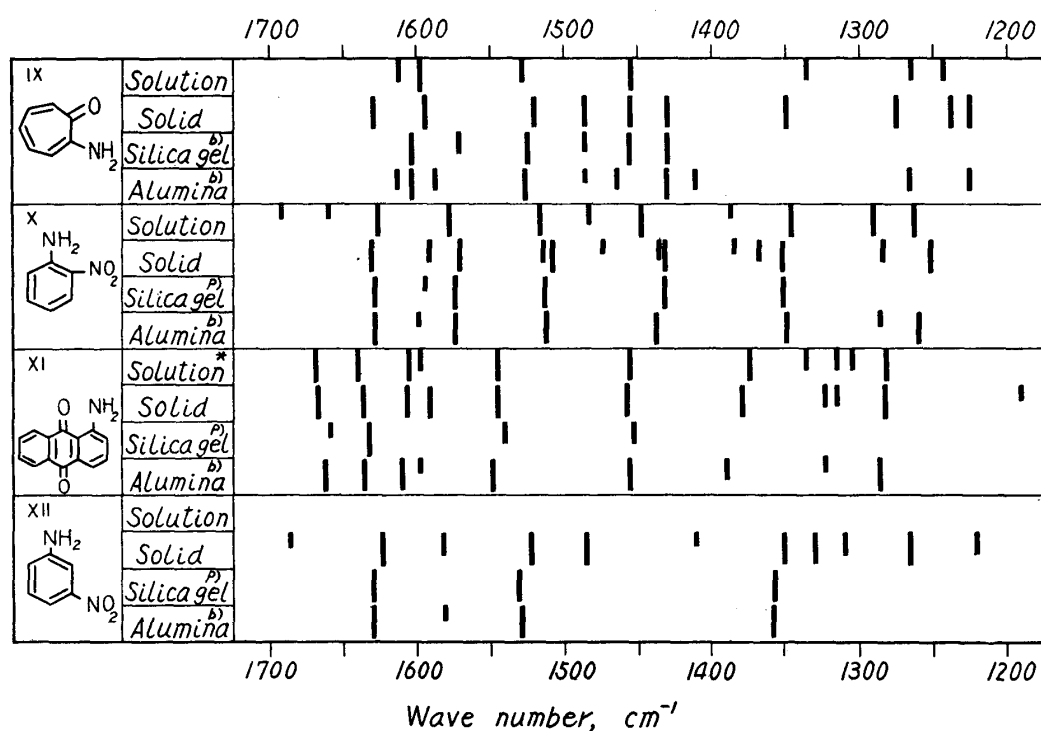


Fig. 5. Position and approximate intensity of the absorption bands of four amines ($1700\sim 1200\text{ cm}^{-1}$ range).

Solution: In carbon tetrachloride (concn. $< 4\%$); except those marked with * which were in chloroform solution.

Solid: As KBr disk

Silica gel: Adsorbed on silica gel

Alumina: Adsorbed on activated alumina

b): Adsorbed from benzene solution

p): Adsorbed from petroleum ether solution

(9) Unpublished data.

(10) L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' (Methuen, 1954), 149.

of acid. The fact that the $\nu(\text{C}=\text{O})$ band in methyl salicylate (VI) and silylamide (VIII) has shifted $20\sim 35\text{ cm}^{-1}$ toward a lower frequency region should be noted.

(2) *Amines*. It has already been shown that the spectra of *o*-nitroaniline (X), indicated in Fig. 2, adsorbed on silica gel or alumina remain almost unchanged from that of pure crystal, and the same can be said of the four compounds illustrated in Fig. 5. Differing from the case of phenolic hydroxyl compounds, there is almost no difference in the spectra according to the adsorbent used, whether silica gel or alumina, and this fact probably signifies that these two kinds of adsorbents have similar mode of adsorbing the amines.

In *m*-nitroaniline (XII), the absorption bands at 1530 and 1350 cm^{-1} corresponding to $\nu(\text{N}-\text{O})$ have both shifted to a higher frequency region than those in the solid and this leaves interesting problem on the state of adsorption that requires further examination with larger number of nitro compounds. In 2-aminotropone (IX), the band for $\delta(\text{N}-\text{H})$ at 1628 cm^{-1} ⁽¹¹⁾ has shifted to a lower frequency region by adsorption on both silica gel and alumina, and the band for $\nu(\text{C}=\text{O})$ at 1594 cm^{-1} in the solid has shifted by 9 cm^{-1} to a higher frequency, coming closer to the value obtained with saturated carbon tetrachloride solution. Earlier report from this

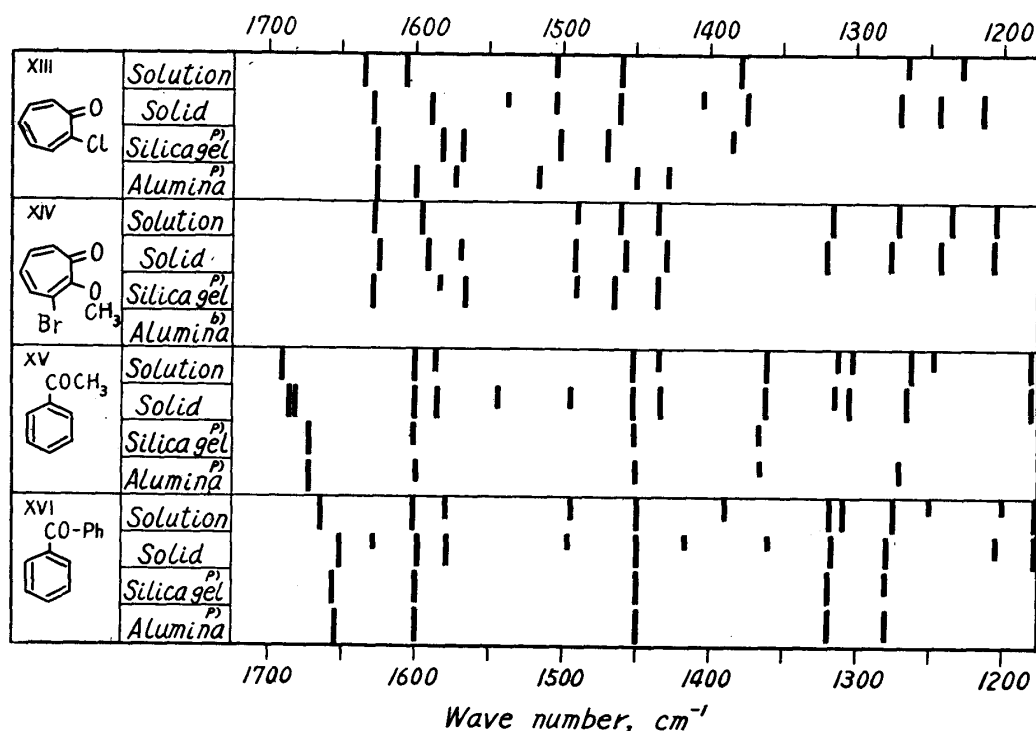


Fig. 6. Position and approximate intensity of the absorption bands of four ketones ($1700\sim 1200\text{ cm}^{-1}$ range).

Solution: In carbon tetrachloride (concn. $<4\%$)

Solid: As KBr disk

Silica gel: Adsorbed on silica gel

Alumina: Adsorbed on activated alumina

b): Adsorbed from benzene solution

p): Adsorbed from petroleum ether solution

(11) Unpublished data. This band was not found in the spectrum of 2-aminotropone- ND_2 .

laboratory⁽¹²⁾ illustrated changes in the absorption bands of $\nu(\text{N-H})$ and $\nu(\text{C=O})$ in 2-aminotropones by intermolecular effect and it is interesting to observe that the adsorbed state tends to become similar to the monomeric form.

(3) *Ketones*. The spectra of four compounds possessing a ketone as the functional group are indicated in Fig. 7. Interest had been felt for the manner of changes in the band for $\nu(\text{C=O})$ in these compounds, but the shift was around 8 cm^{-1} in 2-chloro-tropone (XIII) and 2-methoxy-3-bromotropone (XIV), and this value does not exceed that of $\Delta\nu(\text{C=O})$ between the solid and solution. In these two compounds, the band for $\nu(\text{C=C})$ in the region of $1600\sim 1550\text{ cm}^{-1}$ seems to have made a complicated change, but this band is usually broad and liable to shift easily according to conditions of the measurement in the majority of troponoid compounds, no further argument can be made.

On the other hand, acetophenone (XV) and benzophenone (XVI), possessing a ketone group isolated from the aromatic skeleton, exhibited a great change in the $\nu(\text{C=O})$ band by adsorption and in the case of acetophenone, this band showed a shift of 18 cm^{-1} to the lower frequency by adsorption from 1691 cm^{-1} in solution. The tendency of shift was entirely the same in silica gel and alumina, and this is the same as the result obtained by Sidorov⁽²⁾ with aldehydes and ketones adsorbed on porous silica, probably indicating interaction with OH group on the surface of the adsorbent.

Table 1. Identified frequencies of substances adsorbed on silica gel and in pure state (solid) in the lower frequency region ($900\sim 650\text{ cm}^{-1}$).

Substance	Adsorbed on silica gel	In pure state	Substance	Adsorbed on silica gel	In pure state
Tropolone (I)	cm^{-1} 748	cm^{-1} 754	2-Aminoanthraquinone (XI)	708	707
	724	708	<i>m</i> -Nitroaniline (XII)	738	737
3-Bromotropolone (II)	898	895	2-Chloro-tropone (XIII)	980	975
	739	745		912	901
Phenol (IV)	806	808		868	865
	756	750		776	777
	688	687	667	668	
Benzoic acid (V)	710	706	2-Methoxy-3-bromotropone (XIV)	893	887
	680	683		707	704
	665	664	Acetophenone (XV)	765	759*
Salicylamide (VIII)	745	748	685	688*	
2-Aminotropone (IX)	878	879	Benzophenone (XVI)	768	766
	722	718		702	703
<i>o</i> -Nitroaniline (X)	872	869	* In liquid state.		
	743	748			
	694	698			
	666	663			

(12) S. Kinumaki, Y. Ikegami, and K. Aida, Bull. Chem. Research Inst. Non-aqueous Solutions, Tohoku Univ., 6 (1956), 49 (in Japanese).

(4) *Absorption Bands Appearing in the Lower Frequency Region* (900~650 cm^{-1}). When silica gel is used as the adsorbent, there is no great absorption of the adsorbent in the region below 900 cm^{-1} and this region can be used in observing the spectrum of adsorbed substances, although silica gel exhibits an absorption band of medium intensity at 850 cm^{-1} , so that bands in this region sometimes do not appear clearly.

Table 1 gives data on the frequency of absorption bands observed in substances adsorbed on silica gel in the region of 900~650 cm^{-1} and the values (in solid) of the corresponding pure substances. It would be difficult to find any regularity in the shift of absorption bands by adsorption from these values alone, but in aromatic compounds, absorption bands of strong intensity attributable to C-H out-of-plane deformation appear in this region. It may therefore be concluded that there is no great difference in the infrared absorption in this region between pure crystals and the substance adsorbed, with the exception of tropolone (I) and halogenated troponoids.

Summary

1. Infrared spectra of the adsorbent supporting various substances in column chromatography, with silica gel or activated alumina as the adsorbent, were measured. The regions of 3200~1300 cm^{-1} and 900~650 cm^{-1} can be used for spectral observations of substances adsorbed on silica gel, and in the region of 3100~1200 cm^{-1} for substances adsorbed on alumina. This process is useful for identification of organic compounds and in the study of the mode of adsorption.
2. Phenolic hydroxyl compounds adsorbed on alumina cannot be eluted even with solvents with strong power of desorption, such as ethanol, but their infrared spectra indicate that they are adsorbed almost as an ion; tropolone as its metal complex salts, phenol as $\text{C}_6\text{H}_5\text{-O}^-$, and benzoic acid as $\text{C}_6\text{H}_5\text{-COO}^-$.
3. The spectra of adsorbed *o*- and *m*-nitroaniline are unchanged from that of the corresponding pure substances, within this region. The spectrum of 2-aminotropone is closer to that of solution rather than the solid.
4. The bands for $\nu(\text{C=O})$ in several aromatic ketones show the same tendency in the shift to a lower frequency by adsorption on silica gel or alumina.

Deep gratitude is expressed to Prof. T. Nozoe and members of his laboratory for the supply of valuable samples of troponoid compounds used in this work.