The writer wishes to express his heartiest thanks to Dr. A. F. Benton, whose frequent advice was of great value.

Summary

1. Adsorption measurements have been made for ethylene and hydrogen on a copper catalyst poisoned with carbon monoxide.

2. It has been found that the poison causes a low-pressure increase and a high-pressure decrease of adsorption as compared to measurements made on the unpoisoned catalyst. The poison decreases the catalytic activity very markedly.

3. A possible, general interpretation of the results has been outlined, assuming the process of sorption to comprise a secondary factor such as solution in addition to surface adsorption.

4. It has been shown that carbon monoxide in causing extra, low-pressure sorption of the gases does not leave the hydrogen or ethylene in an activated state.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE PHOTOCHEMICAL REARRANGEMENT OF ACETYLCHLORO-AMINOBENZENE

BY C. W. PORTER AND PAUL WILBUR

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The photochemical rearrangement of acetylchloro-aminobenzene to *p*-chloro-acetanilide has been the subject of many investigations, but heretofore the absorption coefficients in the region of effective radiation have not been determined A study of factors governing the rearrangement in the solid phase has not been made, although Slosson[1] long ago reported the observation that heat alone causes the change. The rearrangement in the presence of various solvents has received careful attention.[2]

We have undertaken to measure the energy required to convert one molecule of the chloro-amine into the isomeric form. As a preliminary step we determined the absorption coefficients of acetylchloro-aminobenzene and of the *p*-chloro-acetanilide over the range between 2200 and 3400 Ångström units. These results, with some observations relating to the rearrangement in the solid phase, are presented in this paper. The energy measurements which have been made on the absorption of certain narrow bands in the spectrum will be published after we have made further attempts to obtain results with pure monochromatic light.

The absorption coefficients were determined as follows. The spectrum

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[1] Slosson, *Am. Chem. J.*, **29**, 289 (1903).

[2] (a) Acree and Johnson, *Am. Chem. J.*, **37**, 258 (1907); (b) Rivett, *Z. physik. Chem.*, **82**, 201 (1913); (c) Mathews and Williamson, THIS JOURNAL, **45**, 2574 (1923).

of the mercury-vapor arc was photographed through a quartz cell containing the pure solvent (conductivity water) and through copper gauze screens. On the same plate, and with equal exposures for corresponding pairs, other series of photographs were made with the screens removed and with the quartz cell filled with solutions of known concentrations of the substance under investigation. The fraction of the total incident light which passed through each screen had been determined in advance by photometric measurements in the visible region. The logarithm of the reciprocal of this ratio is the value of *ecd* in the statement of Beer's law, $I_t/I_0 = 10^{-ecd}$.

Points of equal degrees of blackening on two photographs on the same plate, one taken through a screen of known absorption, and the other through a solution of known concentration, c, and known depth, d, correspond to frequencies where the two systems have the same absorption coefficient, e.

TABLE I

SOLUTIONS OF ACETYLCHLORO-AMINOBENZENE

Plate I: $c = 0.001\ M$			Plate II: $c = 0.0001\ M$		
λ ± 3 Å.	Log $\frac{I_t}{I_0}$	e	λ ± 3 Å.	Log $\frac{I_t}{I_0}$	e
3377	0.159	30	2944	0.31	590
3258	.310	59	2838	.48	914
3189	.480	91	2744	.67	1286
3144	.675	128	2630	.93	1785
3108	.927	178	2562	1.20	2285
3074	1.20	228	2549	1.35	2571
3059	1.35	257	2406	4.80	4571[a]

[a] From Plate IV, $c = 0.00002\ M$.

TABLE II

SOLUTIONS OF *p*-CHLORO-ACETANILIDE

Plate V: $c = 0.001\ M$			Plate VI: $c = 0.0001\ M$		
λ ± 3 Å.	Log $\frac{I_t}{I_0}$	e	λ ± 3 Å.	Log $\frac{I_t}{I_0}$	e
2978	0.159	30	2842	0.31	590
2950	.310	59	2777	.48	914
2934	.480	91	2738	.67	1286
2920	.675	128	2716	.93	1785
2912	.937	178	2699	1.20	2285
2900	1.20	228	2688	1.35	2571

Partial data from Plates VII, VIII, IX, X: $c = 0.00002\ M$

λ ± 3 Å.	$e \times 10^{-2}$	λ ± 5 Å.	$e \times 10^{-2}$	λ ± 10 Å.	$e \times 10^{-2}$
2682	29	2562	99	2340	99
2649	45	2545	114	2308	89
2628	53	2516	128	2283	84
2614	64	2430	142	2253	64
2594	71	2377	128	2242	59
2581	89	2351	114	2230	53

The points of equal densities were determined by projecting the images of the photographic negatives on a vacuum thermopile and finding positions that caused equal galvanometer deflections.[3] The wave lengths corresponding to these points of equal intensities were determined by reference to known lines in the mercury spectrum. In all cases the measurements were made at temperatures between 22 and 25°. The length of the quartz cell containing the solutions was 5.25 cm. The solvent was water. The photographs were taken through a Hilger quartz prism spectrograph.

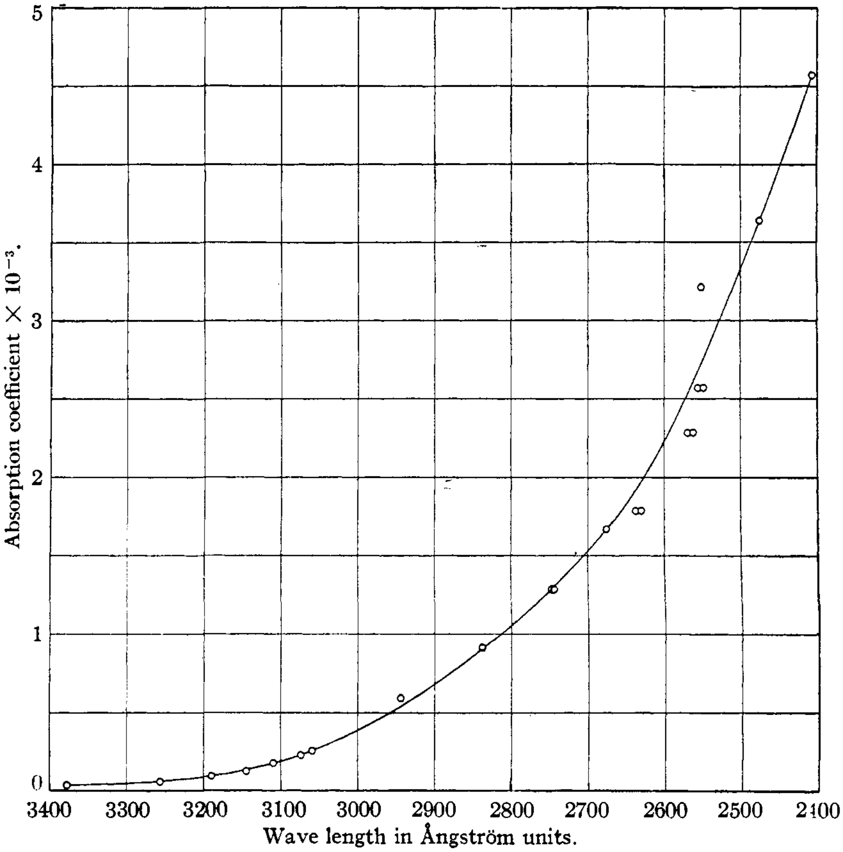

Fig. 1.

These values, together with some data obtained from several other plates, are shown in Figs. 1 and 2. Values referring to points that could not be determined within 10 Å. are, of course, only approximations.

Pure, dry crystals of acetylchloro-aminobenzene, when exposed to the radiation of a mercury-vapor lamp, are converted rapidly into *p*-chloro-

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[3] Ramsperger and Porter, This Journal, **48,** 1267 (1926).

acetanilide. A 90 per cent. conversion was made within eight hours by placing a thin layer of the crystals in an open dish at a distance of 20 cm. below a 220-volt lamp.

The same change can be induced by heat alone. The reaction is slow unless the acetylchloro-aminobenzene is heated to its melting point. Above the melting point the change is rapid, but it is not possible to maintain a constant temperature within the molten mass. The energy of the reaction causes local heating and an acceleration of rate until finally the rearrangement is completed with almost explosive rapidity.

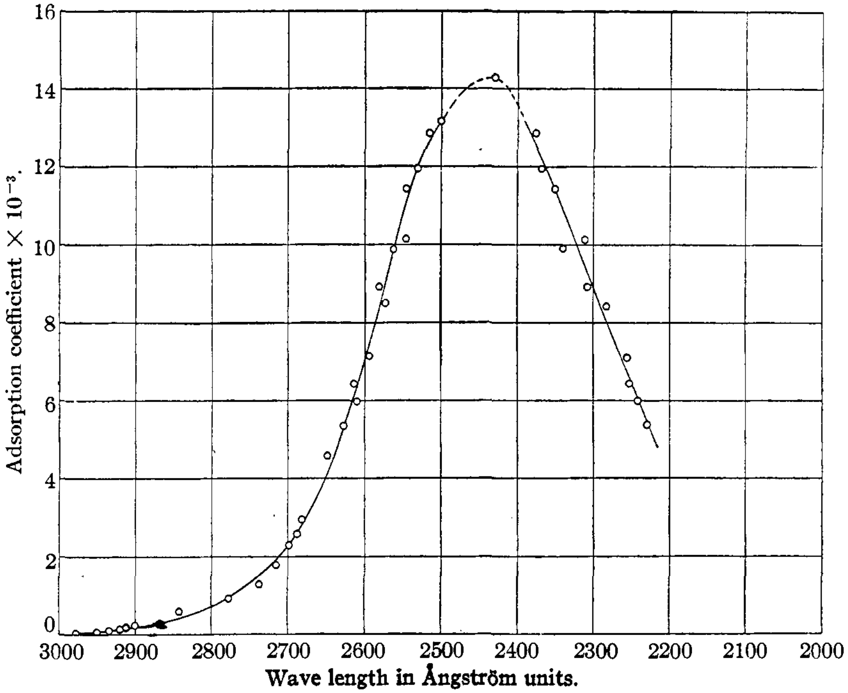

Fig. 2.

Sealed tubes containing the crystalline solid were immersed in a water-bath at 100°. The crystals melted immediately, but within two hours the material had again become solid, due to complete conversion to the higher-melting product. No nitrogen was evolved in the process and, although slight discoloration was sometimes observed, the product was always found to be almost exclusively *p*-chloro-acetanilide.

The claim that the conversion of acetylchloro-aminobenzene into *p*-chloro-acetanilide is actually a rearrangement has been challenged under the assumption that it is a two- or three-stage process.[4] Many

[4] Kipping, Orton and others, *Chem. News*, **108**, 155 (1913).

mechanisms involving the formation of intermediate products with the solvent or with an added catalyst have been proposed.

While these mechanisms may apply to the reaction in the specified environment, they certainly do not describe the behavior of the compound in the dry state. A direct unimolecular exchange of positions between the amino halogen and nuclear hydrogen seems to be the simplest assumption in connection with the photochemical rearrangement of the pure, dry crystals.

Summary

The ultraviolet absorption spectrum of acetylchloro-aminobenzene and of its rearrangement product, *p*-chloro-acetanilide, has been plotted.

The rearrangement is caused by heat alone at comparatively low temperatures. The reaction is completed within two hours at 100°.

The rearrangement occurs in the absence of solvents and without the appearance of a liquid phase when solid crystals of acetylchloro-aminobenzene are exposed to the radiation of a mercury-vapor lamp.

Mechanisms involving intermediate products cannot apply to the solid phase reaction.

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THE CRYSTAL STRUCTURES OF AMMONIUM, POTASSIUM AND RUBIDIUM CUPRIC CHLORIDE DIHYDRATES

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Introduction

The low crystallographic symmetry of most salt hydrates and ammoniates has prevented the study of such compounds by x-ray methods. In an effort to comprehend more fully the geometrical relationship of water to the other components of such compounds we have studied the alkali cupric chloride dihydrates, $R_2CuCl_4.2H_2O$ (where R represents ammonium, potassium or rubidium). These compounds form an apparently isomorphous series crystallizing in the ditetragonal bipyramidal class of the tetragonal system.[1] The axial ratios and observed densities of these compounds are given in Table I.

Large crystals, showing development of (111) and (100), were grown from aqueous solutions containing cupric chloride and the alkali chloride in the correct stoichiometrical quantities. Great caution was used in selecting crystals for the x-ray photographs, since twinning on (111)

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[1] Groth, "Chemische Krystallographie" Engelmann, Leipzig, 1906, vol. I, pp. 355–356.