

when selectively excited tends to give off perceptible intensities of radiation corresponding to every possible mode of molecular motion.

Another aspect of increased rapidity of spreading of energy among the various modes of motion of a gas with increased temperature is that the spectrum of a very hot gas when excited by the electric current tends to show many lines that are invisible when the gas is relatively cool. Thus the spectrum of the mercury arc has no red lines when the vapor is relatively cool, but when the vapor is very hot red lines appear.

W. S. FRANKLIN.

#### NOTES ON ORGANIC CHEMISTRY.

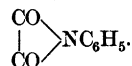
##### THE NITRATION OF ANILINE.

It is generally stated in text-books of organic chemistry that aniline and nitric acid, of tolerably high concentration, yield resinous, tarry, or carbonaceous material from which no definite compounds can be isolated, whereas, in the presence of a large excess of concentrated sulphuric acid, nitration of the aniline takes place without difficulty. This behavior is explained by assuming that in the first case the nitric acid attacks the amino group of aniline more readily than it affects the benzene nucleus, but that the former is 'protected' by the concentrated sulphuric acid.

Several objections can be made to this explanation, among which the following may be mentioned: (1) Aromatic amines form stable compounds (nitrates) with nitric acid, but with nitrous acid the products (nitrites, diazonium derivatives, etc.) are, in general, highly unstable. (2) The primary products of the action of aniline on nitric acid or sulphuric acid are, presumably, aniline nitrate,  $C_6H_5NH_2NO_3$ , and aniline hydrogen sulphate,  $C_6H_5NH_2SO_3H$ , respectively, and it is not apparent why the amino group is less well 'protected' in the former compound than in the latter.

Guided by these and other considerations, we began, some months ago, a study of the action of nitric acid on aniline and on aniline nitrate, and of the behavior of certain derivatives of aniline towards nitric acid alone and

when mixed with acetic acid, oxalic acid, trichloroacetic acid and sulphuric acid, respectively. The aniline derivatives employed included only those in which one or both of the hydrogen atoms of the amino group have been replaced, such as acetanilide,  $C_6H_5NHCOCH_3$ , or oxanilide,



A preliminary account of our work has recently appeared,<sup>1</sup> and we hope to publish further communications on the subject in the course of a few months. The object of this note is to call attention to certain of our results which we think may be of some general interest. Nitric acid of any concentration up to 75.33 per cent. when mixed with aniline in equimolecular proportion forms the nitrate, provided a suitable temperature is maintained, but the slightest excess of acid, if of comparatively high concentration, changes this colorless nitrate to a reddish pink compound. This may be kept for a day or two if it remains sufficiently cool, but, more or less quickly, depending on the temperature and on the excess of acid, it darkens, blackens and may become incandescent. The color is instantly discharged by a drop of water and is regenerated by more acid.

In the formation of mononitro derivatives of the substituted anilines referred to above, the position taken by the nitro group (ortho, meta, para) appears to depend on two factors: (a) the nature of this substituting group, *i. e.*, whether it be negative (acidic), positive (basic), or neutral; (b) the strength, not concentration, of the acid which has been mixed with the nitric acid. Should this conclusion be justified by our subsequent experiments, it will be seen that, as we can vary each of the above factors between very wide limits, the possibility is afforded of varying *a* in the same direction as *b* or in an opposite one, in order to prepare some desired isomer. Moreover, similar conditions might reasonably be expected to apply to the nitration of compounds in general, and if to nitration, then also, so far as experi-

<sup>1</sup>*Amer. Chem. Jour.*, **36**, 605 (1906).

mental conditions permit, to other similar reactions involving substitution.

We desire to call special attention to the discovery that acetic acid and sulphuric acid play a definite part in determining the position of the entering nitro group, because, heretofore, the belief has been quite general that when present with nitric acid the function of the sulphuric acid was confined to withdrawing from the sphere of activity the water formed during the process of nitration, while the acetic acid was regarded as a diluent to reduce the activity of the nitric acid. Oxalic acid and trichloroacetic acid do not appear to have been previously employed in nitration experiments.

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#### NOTES ON THE HISTORY OF NATURAL SCIENCE.

SIR JOHN MANDEVILLE.

To that dauntless literary freebooter of the fourteenth century who styled himself Sir John Mandeville, and whose 'Voiage and Travaile' enjoyed for a long time enormous popularity, very little consideration is given by historians of natural science. Yet this extraordinary compilation contains many matters of interest to the zoologist, botanist and even geologist of our day, to say nothing of its value from a purely literary or philological standpoint.

A fruitful theme for investigation has been an analysis of the sources, contemporary, early medieval and ancient, from which the narrator made wholesale robberies. Claiming to have been the traveling companion of Friar Odoric, the Bohemian (1286-1331), he appropriated bodily large portions of that noted traveler's itinerary, and precisely these portions are of chief interest to the naturalist. Concerning this question of sources, one may consult the splendid bilingual edition published by the Roxburghe Club, with notes by Mr. Warner, of the British Museum, and the valuable essay by Albert Bovenschen, published by the Berlin Geographical Society in 1888.

A point of interest to the geologist is Sir John's mention, in chapter 8, of the eruptive condition of Etna and the Lipari Isles. Very incomplete records have been preserved of early Liparian eruptions, and it would be interesting to find the statement confirmed by other writers that 'there be seven swelges that burn.' In the original French version this passage concludes: "Et de Ytaille iusques a ces volcans nad plus de xxv. lieuez; et dit homme qe ces sunt chymenes denfern." This last remark is evidently a localization of a familiar legend, but whether original or not on the part of the author is hard to say. A parallelism exists, though I am not aware of any one having called attention to it, with one of the 'Dialogues' of St. Gregory, where the hermit of Lipari is described as having seen Theodoric the Great, on the day of his death, carried in bonds between Pope John and Symmachus, and thrown into the Volcano of Lipari. It was also a popular belief during the middle ages that Charles Martel had been banished within the crater of Stromboli.

Concerning the animal lore scattered throughout Sir John's book, it has been observed that "all the old legends of the Alexander saga and of the 'Miracles of the Orient'<sup>1</sup> are here amalgamated with much that is new about those fabulous monsters with which the medieval fancy populated the mysterious East." Yet besides these fables there is much authentic information of real value. A single point, of minor interest to be sure, is worth mentioning on account of its having engaged Cuvier's attention. A curious subversion of the Andromeda legend occurs in chapter 5 of Mandeville's book, where it is said that one of the ribs of the monster found at Joppa measured forty feet in length. The statement is evidently borrowed from Solinus (chapter 34), who obtained his information in turn from Pliny ('Nat. Hist.' v. 14; ix., 4). According to the latter, the total length of the creature, whose bones were conveyed to Rome and exhibited there, was forty feet; and as shown by Cuvier, the description could not have applied to any other animal than a whale.

<sup>1</sup> References to the spread of this literature are given in SCIENCE, Vol. 23, p. 195.