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Amination of Benzoic Acid in the γ-Radiolysis of Liquid Ammonia

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Ammonia and aqueous ammonia solutions of benzoic acid, ^{14}C-carboxyl labeled, were irradiated with ^{60}Co γ-rays at absorbed doses of 1.9×10^{20} and 4.4×10^{20} eV/g respectively. The irradiation temperature was 0°C in both cases. An isotope dilution method was applied to measure the products in irradiated solutions. The G values of *o*-, *m*-, and *p*-aminobenzoic acids were 0.016, 0.022, and 0.027 respectively in an ammonia solution. On the other hand, the G values of products in an aqueous ammonia solution were 0.011, 0.013, and 0.017 for *o*-, *m*-, and *p*-aminobenzoic acids and 0.029, 0.033, and 0.040 for *o*-, *m*-, and *p*-hydroxybenzoic acids. The disappearance of benzoic acid in an ammonia solution corresponded to a G value of about 1.46. From the ratio of the relative partial rate factors, it was deduced that the aminating agent was the amino radical in both cases.

The amination of aromatic compounds has been fairly extensively investigated by using hydroxylammonium chloride in the presence of Friedel-Crafts catalysts,[1] hydroxylamine-*O*-sulfonic acid and some of its derivatives,[2,3] and hydroxylamine-titanous ion in an acid solution.[4] On the other hand, aromatic amination induced by ionizing radiation has received relatively little attention.

The products from radiolysis of liquid ammonia are similar to those from liquid water.[5] The

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[1] C. Graebe, *Ber.*, **34**, 1778 (1901).

[2] R. N. Keller and P. A. S. Smith, *J. Am. Chem. Soc.*, **68**, 899 (1946).

[3] P. Kovacic and R. P. Bennett, *ibid.*, **83**, 221 (1961).

[4] H. Seaman, P. J. Taylor and W. A. Waters, *J. Chem. Soc.*, **1954**, 4690.

[5] D. Cleaver, E. Collinson and F. S. Dainton, *Trans. Faraday Soc.*, **56**, 1640 (1960); F. S. Dainton, T. Skwarski, D. Smithies and E. Wezranowski, *ibid.*, **60**, 1068 (1964); L. Kolditz and U. Prösch, *Z. physik. Chem.*, **218**, 109 (1961).

amination in the nucleus of aromatic compounds, therefore, may be expected to occur during the irradiation of its ammonia solution with ionizing radiation. Puig and Schwarz[6] studied the radiolysis of an ammonia solution of benzene with ^{60}Co γ-rays and found aniline to be formed, corresponding to phenol in an aqueous solution, with a G value of 0.55.

In the mono-substitution of mono-substituted benzene derivatives, the ratio of the products depends upon the degree to which the substituent displays electron-withdrawing or electron-donating properties. The carboxyl group of benzoic acid is particularly interesting as an aromatic substituent because of its *meta*-directional effect on an attacking reagent for the aromatic nucleus. Consequently, some information about an attacking species may be obtained by investigating the ratio of the isomers of substituted benzoic acid.

The aim of this work has been to elucidate the attacking species concerned in the amination reaction in the γ-radiolysis of ammonia solutions. Some results obtained by irradiating ammonia and aqueous ammonia solutions of ^{14}C-carboxyl labeled benzoic acid at a relatively high dose will be described. The reaction products were determined by means of an isotope dilution method. On the basis of the isomeric distribution of the aminobenzoic acids thus obtained, the attacking species participating in the amination reaction in the aromatic nucleus of benzoic acid will be deduced.

Experimental

Materials. The liquid ammonia used was purified in the following manner. An aqueous ammonia solution was placed in a 1 *l* round-bottomed flask fitted with a reflux condenser. The flask was then heated slowly in a water bath. The ammonia gas evolved, after passing through the condenser, was introduced into columns packed with soda-lime and sodium hydroxide; then it was collected into a storage vessel cooled by dry ice-acetone and stored at least for 15 hr as a liquid over metallic sodium. Just before use as a solvent, the ammonia in the storage vessel was distilled under diminished pressure into another vessel immersed in dry ice-acetone in order to eliminate any residual metallic sodium and any other solid impurities; it was then distilled three more times in order to remove any hydrogen formed during purification by metallic sodium.

The water used had been triply distilled, the final distillation being from alkaline potassium permanganate.

The non-radioactive acids used as the carriers of the isotope dilution method were obtained from commercial sources. All of these acids were GR grade and had then been purified further by recrystallization.

Benzoic acid, ^{14}C-carboxyl labeled, was purified by recrystallization from ethyl alcohol - water and then diluted to the specific activities of 1.41×10^{10} dpm/mol and 3.40×10^{10} dpm/mol respectively.

Preparation of Solutions. In an irradiation vessel there was placed 150 mg of ^{14}C-labeled benzoic acid, with a specific activity of 1.41×10^{10} dpm/mol. Then the vessel was connected to a vacuum line and carefully degassed. After the degasification, 1.52 mol of liquid ammonia, purified by the method described above, was distilled under diminished pressure into a vessel cooled by dry ice-acetone. Then the irradiation vessel with an ammonia solution, cooled by liquid nitrogen, was sealed off.

An aqueous ammonia solution of benzoic acid was prepared by distillating 0.88 mol of liquid ammonia into an irradiation vessel already containing an aqueous benzoic acid solution which had been prepared by adding 150 mg of ^{14}C-labeled benzoic acid (with a specific activity of 3.40×10^{10} dpm/mol) to 0.83 mol of triply-distilled water which has been degassed by repetitions of the freezing-pumping process.

Irradiation. A ^{60}Co γ-rays source of about 16 kCi was used. The ammonia solution was irradiated at the absorbed dose of 1.9×10^{20} eV/g and at the dose rate of 3.5×10^{17} eV/g/min. The total dose given to an aqueous ammonia solution was 4.4×10^{20} eV/g at the dose rate of 6.7×10^{17} eV/g/min. The irradiation temperature of both samples was 0°C, which was controlled with ice-water. The dose rate was measured by Fricke dosimetry, taking $G(\text{Fe}^{3+})$ to be 15.5. Appropriate corrections were made for the difference in the electron densities of liquid ammonia and water.

Radioactive Assay. After irradiation, the breakseal of the irradiation vessel was broken. The contents were transferred to a beaker immersed in liquid nitrogen. The irradiation vessel was washed with about 10 cc of demineralized water. After it had stood overnight in order to evaporate any excess ammonia, the combined aqueous solution was diluted to a total volume of 25 cc with demineralized water. An aliquot of the diluted solution was then thoroughly mixed with an accurately-weighed quantity of the carrier acid in ethyl alcohol. The solution was evaporated to dryness, and the precipitate was purified by recrystallization from a suitable solvent until a constant counting rate was obtained. The aminobenzoic acids in products were derived to acetoamidobenzoic acids and purified.

An aliquot of a purified sample was dissolved in the solution of 10 cc of liquid scintillant (4 g of PPO (2,5-diphenyloxazole), 100 mg of POPOP (1,4-bis-2-(5-phenyloxazole)benzene)/*l* of toluene) and 5 cc of methyl alcohol and then counted in a Packard 314 EX-type liquid scintillation spectrometer assembly. A liquid scintillant solution of ^{14}C-labeled benzoic acid (with a specific activity of 3200 dpm/mg) was used as the internal standard for the determination of the counting efficiency.

Results

An ammonia solution of ^{14}C-labeled benzoic acid was irradiated with ^{60}Co γ-rays, and the amount of remaining benzoic acid and the presence of the three mono-aminobenzoic acids and 2,2′-biphenyldicarboxylic acid in the irradiated solution were confirmed by a radioactive-tracer technique. The yield and the G value of each reaction product obtained are summarized in Table 1.

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[6] J. R. Puig and E. Schwarz, *Industrial Uses of Large Radiation Source,* **1,** 57 (1963).

TABLE 1. PRODUCTS IN γ-RADIOLYSIS OF AMMONIA SOLUTION OF BENZOIC ACID

	Amount mol	Yield %	G
o-Aminobenzoic acid	$(1.31\pm0.06)\times10^{-6}$	0.11	0.016
m-Aminobenzoic acid	$(1.74\pm0.05)\times10^{-6}$	0.14	0.022
p-Aminobenzoic acid	$(2.18\pm0.07)\times10^{-6}$	0.18	0.027
2,2′-Biphenyldicarboxylic acid	$(4.47\pm0.25)\times10^{-7}$	0.07	0.0055
Benzoic acid*1	$(1.110\pm0.003)\times10^{-3}$	90.4	
−Benzoic acid*2	$(1.18\pm0.03)\times10^{-4}$	9.6	1.46

Dose, 1.9×10^{20} eV/g, dose rate, 3.5×10^{17} eV/g/min.
Irradiation temperature, 0°C.
*1 Remaining benzoic acid.
*2 Amounts of the disappearance of benzoic acid.

TABLE 2. YIELDS OF AMINOBENZOIC AND HYDROXYBENZOIC ACIDS IN γ-RADIOLYSIS OF AQUEOUS AMMONIA SOLUTION

	Amount mol	Yield %	G
o-Aminobenzoic acid	$(1.20\pm0.06)\times10^{-6}$	0.10	0.011
m-Aminobenzoic acid	$(1.45\pm0.03)\times10^{-6}$	0.12	0.013
p-Aminobenzoic acid	$(1.84\pm0.04)\times10^{-6}$	0.15	0.017
o-Hydroxybenzoic acid	$(3.22\pm0.08)\times10^{-6}$	0.26	0.029
m-Hydroxybenzoic acid	$(3.67\pm0.03)\times10^{-6}$	0.30	0.033
p-Hydroxybenzoic acid	$(4.42\pm0.14)\times10^{-6}$	0.36	0.040

Dose, 4.4×10^{20} eV/g, dose rate, 6.7×10^{17} eV/g/min.
Irradiation temperature, 0°C.

The remaining benzoic acid in the irradiated solution, 1.11×10^{-3} mol was recovered. This corresponds to 90.4 per cent of the initial amounts of the acid. Consequently, the amount of the total reaction of benzoic acid is 1.18×10^{-4} mol and the G value of the disappearance of the acid, shown as −benzoic acid in Table 1, is calculated to be 1.46. The G value of 1.46 is smaller than that obtained in the case of an aqueous solution of benzoic acid.[7] The G value for mono-aminobenzoic acids were: *ortho,* 0.016; *meta,* 0.022; and *para,* 0.027. The total G value is 0.065, only about a quarter of that of the mono-hydroxybenzoic acids obtained in an aqueous solution.

When the irradiation of an aqueous ammonia solution of benzoic acid was carried out at an absorbed dose of 4.4×10^{20} eV/g, isomers of mono-aminobenzoic acids and of mono-hydroxybenzoic acids were observed as products. The yields are given in Table 2. The total yield of mono-aminobenzoic acids was about 4.5×10^{-6} mol, while that of mono-hydroxybenzoic acids was about 1.1×10^{-5} mol. Therefore, the ratio of mono-aminobenzoic acid to mono-hydroxybenzoic acids is about 1 : 2.4.

From Table 2, the G value of mono-aminobenzoic acids in an aqueous ammonia solution can be seen to be 0.041. In spite of the low G value of mono-aminobenzoic acids in an aqueous ammonia solution, the G value ratio, calculated to be 0.65 : 0.76 : 1 for *o*- : *m*- : *p*-isomers, agrees fairly well with that of 0.59 : 0.81 : 1 in an ammonia solution. The total G value of the mono-hydroxybenzoic acids was 0.10. Although this value is less than a half of that obtained in an aqueous solution, the *o*- : *m*- : *p*-isomer ratio, 0.73 : 0.83 : 1, was similar to that, 0.72 : 0.84 : 1, obtained in an aqueous solution.[7]

Discussion

When an ammonia or aqueous ammonia solution of benzoic acid is subjected to irradiation with ionizing radiation, there is the possibility of some reactions in addition to the amination of the acid. The decarboxylation of ^{14}C-labeled benzoate occurred during the irradiation of a dilute, aerated aqueous solution by ^{60}Co γ-rays.[8,9] Therefore, it may be assumed that a similar decarboxylation occurs in the irradiation of an ammonia solution of benzoic acid. However, no carbon dioxide was measured in this work.

In the γ-radiolysis of an aqueous benzoic acid solution, the ratio of the mono-hydroxybenzoic

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[7] A. Sakumoto and G. Tsuchihashi, This Bulletin, **34**, 663 (1961).

[8] A. M. Downes, *Austr. J. Chem.*, **11**, 154 (1958).

[9] R. W. Matthews and D. F. Sangster, *J. Phys. Chem.*, **69**, 1938 (1965).

acids to biphenyldicarboxylic acids produced was about 1 : 3.[7] However, in the γ-radiolysis of an ammonia solution of benzoic acid, the *G* value of 2,2′-biphenyldicarboxylic acid, the most abundant isomer in an aqueous solution, was smaller than that of any isomer of mono-aminobenzoic acids shown in Table 1. The reason for this is not obvious. When an aqueous solution of *p*-aminobenzoic acid was irradiated with X-rays, 3-hydroxy-4-aminobenzoic acid was observed as the main product, while *p*-hydroxybenzoic acid and aniline were also produced in trace amounts.[10] Therefore, as the production of mono-aminobenzoic acids increases, the similar reaction of the acids will gradually increase in ammonia and aqueous ammonia solutions.

In order to understand the amination reaction of the aromatic nucleus of benzoic acid in the γ-radiolysis of ammonia solutions, consideration must be given to the possibility that the reaction products of the acid with reactive species produced in the γ-radiolysis of ammonia might give aminobenzoic acids. When the pulse radiolysis of an alkaline solution of benzoic acid was carried out using a 15 MeV electron pulse, the acid readily reacted with the hydrated electron produced by the irradiation.[11,12] Nitrobenzene, in which the nitro group has the *meta*-directional effect, also reacted readily with the hydrated electron.[13,14] The hydrated electron scavengers have little or no effect on the yield of *o*-nitrophenol produced in the γ-radiolysis of an aqueous nitrobenzene solution.[15] This means that the product of the electron-nitrobenzene reaction is not a precursor of nitrophenols. Therefore, it may be assumed that there is little possibility of the reaction product of benzoic acid with the solvated electron giving aminobenzoic acids when an ammonia solution is irradiated with ^{60}Co γ-rays.

One of several methods for obtaining information on the attacking reagent involved in a radiation-induced amination reaction is to study the partial rate factors for amination in the nucleus of benzoic acid. It has been evident[16] that, in the further substitution reaction of the mono-substituted benzene derivatives, C_6H_5X, in which the substitutent X is assigned to a $-E$ effect such as that of the carboxyl group, if the entering substituent is an electrophilic heterolytic reagent (*e.g.*, NO_2^+) the partial rate factor at the *meta*-positions with respect to the substituent already present is larger than that at the *ortho*- and *para*-positions. On the other hand, if the mono-substituted benzenes are attacked by a homolytic reagent such as the phenyl radical, a large partial rate factor is obtained at the *ortho*- and *para*-positions rather than at the *meta*-positions. Therefore, a comparison of the partial rate factors will offer information about the attacking reagent participating in the substitution reaction.

When an ammonia solution of benzoic acid was irradiated at the absorbed dose of 1.9×10^{20} eV/g, the amounts of mono-aminobenzoic acids were: *ortho*, 1.31×10^{-6} mol (0.11 per cent of the theoretical amount); *meta*, 1.74×10^{-6} mol (0.14 per cent); *para*, 2.18×10^{-6} mol (0.18 per cent). Unfortunately, the partial rate factor itself for the amination reaction at each nuclear position of benzoic acid can not be obtained from these values. However, in the mono-substituted benzene, C_6H_5X, the partial rate factors at *o*-, *m*-, and *p*-positions with regard to the substituent X are given by the three following expressions respectively:

$$
\begin{aligned}
{}^{\mathrm{X}}_{\mathrm{H}}k_o &= 6\cdot{}^{\mathrm{X}}_{\mathrm{H}}K\cdot(o)/2\\
{}^{\mathrm{X}}_{\mathrm{H}}k_m &= 6\cdot{}^{\mathrm{X}}_{\mathrm{H}}K\cdot(m)/2\\
{}^{\mathrm{X}}_{\mathrm{H}}k_p &= 6\cdot{}^{\mathrm{X}}_{\mathrm{H}}K\cdot(p)
\end{aligned}
$$

where (o), (m), and (p) represent the yield of the respective isomers of the reaction products. Therefore, it is possible to use the yield of mono-aminobenzoic acids as a measure of the partial rate factor of the amination reaction at any position in the aromatic nucleus of benzoic acid, if the isomeric distribution accurately reflects the extent of attack by the reagent on the three different positions of benzoic acid. In the case of a radiation-induced reaction, it is preferable to use the *G* value, used as a measure of the radiation-chemical yields, rather than chemical yields of products. Then, using the *G* value thus obtained, the relative partial rate factors were calculated to be 0.008, 0.011, and 0.027 for $(o)/2$, $(m)/2$, and (p) in an ammonia solution, as is shown in Table 3. The relative partial rate factor at the *para*-position was larger than that at the *meta*-position. This result demonstrates that the attacking species in amination is uncharged.

Yoshida, Matsumoto, and Oda[17] have reported on the amination of benzoic acid using the hydroxylamine-ferrous ion, which is well known as an aminating reagent with the amino radical. The values they obtained are also presented in Table 3 for the sake of comparison. In this amination, if an aqueous solution of hydroxylamine-ferrous

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[10] K. F. Nakken, *Radiation Res.*, **21**, 446 (1964).

[11] A. Szutka, J. K. Thomas, S. Gordon and E. J. Hart, *J. Phys. Chem.*, **69**, 289 (1965).

[12] D. F. Sangster, *ibid.*, **70**, 1712 (1966).

[13] E. J. Hart, S. Gordon and J. K. Thomas, *ibid.*, **68**, 1271 (1964).

[14] M. Anbar and E. J. Hart, *J. Am. Chem. Soc.*, **86**, 5633 (1964).

[15] R. W. Matthews and D. F. Sangster, *J. Phys. Chem.*, **71**, 4056 (1967).

[16] D. H. Hey, "Vistas in Free-Radical Chemistry," ed. by W. A. Waters, Pergamon Press, London (1959), p. 209.

[17] Z. Yoshida, T. Matsumoto and R. Oda, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)* **65**, 46 (1962).

TABLE 3. RELATIVE PARTIAL RATE FACTORS OF AMINATION IN AROMATIC NUCLEUS OF BENZOIC ACID

	Solvent	(*o*)/2	(*m*)/2	(*p*)
γ-Radiolysis	NH_3	0.008	0.011	0.027
	NH_3-H_2O*1	0.011	0.013	0.033
NH_2OH-Fe(II)*2	H_2O	0.4	0.8	1.2
	96% H_2SO_4	1.45	2.05	3.8

*1 Values from *G* value calculated from the amount of energy absorbed in ammonia in aqueous ammonia solution.

*2 See Ref. 17.

ion was used, 52 per cent of the aminobenzoic acids produced were poly-aminobenzoic acids. On the other hand, if the solvent was 96 per cent sulfuric acid, the poly-aminobenzoic acids composed only 0.9 per cent of the aminobenzoic acids. In spite of this difference in the ratio of poly-aminobenzoic acids to aminobenzoic acids, the large relative partial rate factor was obtained at the *para*-position rather than at the *meta*-position in both cases. It is also clear from Table 3 that the ratio of the relative partial rate factor obtained in the γ-radiolysis of an ammonia solution agrees fairly well with that obtained in amination using the hydroxylamine-ferrous ion.

The reaction rate constants of the hydroxyl radical with the substituted benzenes, C_6H_5Y, are larger than those of the hydroxyl radical with benzene, regardless of Y substituent, if the Y substituent is an electron-donating group.[18] Therefore, it may be assumed that the amination of mono-aminobenzoic acids is easier than that of benzoic acid in the γ-radiolysis of an ammonia solution. When the irradiation of an aqueous benzoic acid solution was carried out, di-hydroxybenzoic acids composed about 15 per cent of the mono-hydroxybenzoic acids, even under conditions favorable for hydroxylation.[7] Accordingly, it is reasonable to presume that there is little formation of poly-aminobenzoic acids in the range of the irradiation. No poly-aminobenzoic acids were measured, so the results obtained cannot be used as an accurate measure of the partial rate factors in the amination reaction. However, it can be deduced from the ratios of the relative partial rate factors summarized in Table 3 that the attacking reagent concerned in the amination reaction during the irradiation of an ammonia solution of benzoic acid is the amino radical.

Returning now to the irradiation of an aqueous ammonia solution of benzoic acid, a lower *G* value of aminobenzoic acids was obtained than that in an ammonia solution. In an aqueous solution of ammonia, the ammonia molecule and the water molecule are attracted to each other by the hydrogen bond, which is roughly 5 per cent of the energy of a covalent bond.[19] Since the energy of activation of such a bond is small, the bond forms and breaks with ease at ordinary temperatures. In a 0.1 molar solution of ammonia, only about a half of the ammonia molecules are hydrated, and although it is possible to isolate two stable crystalline hydrates, $NH_3 \cdot H_2O$ and $(NH_3)_2 \cdot H_2O$, at low temperatures, there is no evidence that undissociated NH_4OH is present.[20] Therefore, it may be assumed that the amount of energy absorbed in each component in an aqueous solution of ammonia is proportional to the total number of electrons in each component when such a solution is irradiated with ^{60}Co γ-rays. Now, by assuming that only ammonia is involved in the formation of aminobenzoic acids in such a solution, the amount of the acids should be related to the amount of energy absorbed in ammonia in the mixture. The determination of the *G* values of hydroxybenzoic acids was also performed in the same manner by assuming that only water is involved in the formation of the acids. The *G* values calculated were 0.021, 0.026, and 0.033 for *o*-, *m*-, and *p*-aminobenzoic acids and 0.060, 0.069, and 0.083 for *o*-, *m*-, and *p*-hydroxybenzoic acids, respectively.

The total *G* value of the aminobenzoic acids was calculated to be 0.080. This value is about 23 per cent larger than that obtained in an ammonia solution. These two *G* values should be in accord with each other provided there is no interaction between the ammonia and water involved in the reaction. The above difference in *G* value, therefore, suggests that there is some interaction between ammonia and water in such a mixture. This suggestion is supported by the enhancement of hydrazine in the γ-radiolysis of an aqueous solution of ammonia.[21] From the proton affinity[22] for ammonia, the proton transfer to ammonia may be expected to occur. If the neutralization of the produced NH_4^+ by solvated electrons were to

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18) M. Anbar, D. Meyerstein and P. Neta, *J. Phys. Chem.*, **70**, 2660 (1966).

19) J. B. Davis, *J. Chem. Educ.*, **30**, 511 (1953).

20) F. A. Cotton and G. Willkinson, "Advanced Inorganic Chemistry, A Comprehensive Text, 2nd Ed.," John Wiley and Sons, New York (1966).

21) A. Sakumoto, This Bulletin, **39**, 1349 (1966).

22) J. O'M. Bockris and B. E. Conway, "Modern Aspects of Electrochemistry, No 3," Butterworths, London (1964).

produce amino radicals,[23] some increase in the yields of aminobenzoic acids can be explained. On the other hand, the G value of hydroxybenzoic acids was calculated to be 0.212, slightly less than that obtained in an aqueous solution. Consequently, there might be the possibility of the following interaction:[24]

$$NH_3 + \cdot OH \rightarrow \cdot NH_2 + H_2O$$

If the amino radical is the attacking reagent participating in the amination reaction in an aqueous ammonia solution, the ratio of the relative partial rate factors may be in accord with that obtained in an ammonia solution. On the basis of the assumption that the amount of aminobenzoic acid is proportional to the amount of energy absorbed in ammonia in an aqueous ammonia solution, the relative partial rate factors, $(o)/2$, $(m)/2$ and (p), in such a solution were calculated to be 0.011, 0.013 and 0.033 respectively, as is shown in Table 3. The $(o)/2 : (m)/2 : /(p)$ ratio, 0.32 : 0.38 : 1, is in striking agreement with the ratio, 0.30 : 0.41 : 1, obtained in an ammonia solution. Therefore, it is possible to deduce that the attacking species involved in the amination reaction in an aqueous ammonia solution is also the amino radical.

The ratio of the G value of *m*-aminobenzoic acid to that of *p*-aminobenzoic acid was less than 2. This is attributable to some degree of electrophilic character of the amino radical.

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[23] F. T. Jones and T. J. Sworski, *Trans. Faraday Soc.*, **63**, 2411 (1967).

[24] Yu A. Sorokin, V. I. Tsivenko and S. Ya. Pshezhetskii, *Zhur. fiz. Khim.*, **37**, 1871 (1963).