BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (7), 2025 (1976)

Origin of the Oxygen Atom in the Nitrosomesitylene Formed by the Oxidation of Mesidine with Fremy's Salt

Tomoji TAKAHASHI, Hiroshi MINATO, and Michio KOBAYASHI
Department of Chemistry, Tokyo Metropolitan University, Setagaya, Tokyo 158

(Received March 6, 1976)

Synopsis. The mechanism of the oxidation of aromatic amines with Fremy's salt was investigated by use of ^{18}O-labelled compounds. It was shown that the nitroso-oxygen atom originates not from water but from the nitroxide oxygen and sulfonate oxygen atoms of Fremy's salt.

Usually it is not possible to isolate nitroso compounds by the oxidation of aromatic amines, but such sterically hindered amines as mesitylenamine give nitroso compounds in good yields by the treatment with Fremy's salt.[1] However, the mechanism of this reaction has not been elucidated yet. We have investigated the mechanism of this reaction by use of ^{18}O-labelled Fremy's salt.

Fremy's salt[nitroxide-^{18}O] was prepared according to the following steps.

$$\text{NaOH} + \text{H}_2{}^{18}\text{O (large excess)} \longrightarrow \text{Na}^{18}\text{OH}$$

$$2\text{Na}^{18}\text{OH} + \text{NOCl} \longrightarrow \text{NaN}^{18}\text{OO} + \text{H}_2{}^{18}\text{O} + \text{NaCl}$$

$$\text{NaN}^{18}\text{OO} + 2\text{KHSO}_3 \longrightarrow \text{H}^{18}\text{O-N(SO}_3\text{K)}_2 + \text{NaOH}$$

$$6\text{H}^{18}\text{O-N(SO}_3\text{K)}_2 + 2\text{KMnO}_4 \longrightarrow 3[{}^{18}\dot{\text{O}}\text{-N(SO}_3\text{K)}_2]_2 + 2\text{MnO}_2 + 2\text{KOH} + 2\text{H}_2\text{O}$$

The excess ^{18}O atom% of Fremy's salt[nitroxide-^{18}O] prepared using $H_2{}^{18}O$ (excess ^{18}O, 1.3 atom%) was 0.104±0.009%, and hence the excess ^{18}O atom% in the nitroxide oxygen must be 0.728±0.06%, which roughly corresponds with the value calculated (0.65%) from the excess ^{18}O atom % of the heavy water used (1.3%). This shows that no oxygen exchange with solvents occurred during the above reactions.

The preparation of Fremy's salt[sulfonate-^{18}O] was attempted by the reaction between $NaNO_2$ and $KHS^{18}OO_2$ (obtained from $K^{18}OH$ and SO_2), but the salt prepared contained only 0.004 excess ^{18}O atom %. This suggests that rapid oxygen exchange with water took place. A separate experiment showed that sulfite ions readily exchange oxygen atoms with water under strongly alkaline conditions. Therefore, the above results can be rationalized by assuming that $KHS^{18}OO_2$ reacted with water faster than with $NaNO_2$.

The experimental results of the reaction between mesitylenamine and Fremy's salt may be summarized as follows:

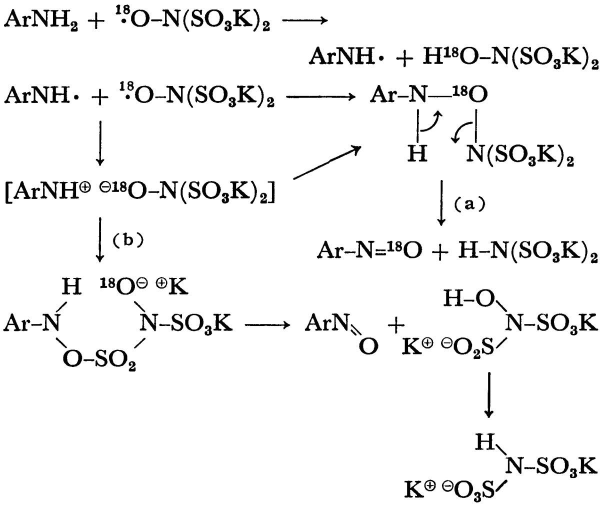
1) When mesitylenamine was oxidized with unlabelled Fremy's salt in acetone–$H_2{}^{18}O$ (1.3 excess atom %), the nitrosomesitylene obtained possessed only 0.002±0.001 excess ^{18}O atom %. Thus no ^{18}O-incorporation from $H_2{}^{18}O$ took place.

2) When mesitylenamine was oxidized with Fremy's salt[nitroxide-^{18}O] in acetone–H_2O, the nitrosomesidine obtained possessed 0.253±0.03 excess ^{18}O atom %.

3) When mesitylenamine was oxidized with Fremy's salt[nitroxide-^{18}O] in dioxane–H_2O, the nitrosomesitylene obtained possessed 0.216±0.005 excess ^{18}O atom %.

The above results clearly show that the oxygen atom of the nitrosomesitylene does not come from water but from Fremy's salt.

If the nitroxide oxygen atom of Fremy's salt directly becomes the nitroso oxygen of the nitrosomesitylene, the excess ^{18}O atom % of the nitrosomesitylene must be the same as that of the nitroxide oxygen of Fremy's salt (0.728±0.06%). However, the value found was only about 1/3 of it. The possibility that the ^{18}O atoms of the nitrosomesitylene formed are lost by subsequent exchange with water can be rejected from our findings[2] that the oxygen atoms of aromatic nitroso compounds virtually do not exchange with water under neutral or strongly acidic conditions. Therefore, the oxygen atom of the nitrosomesitylene comes from both the nitroxide oxygen and the sulfonate oxygen atoms. A plausible mechanism is the following.



In the course (a) the nitroxide oxygen is converted directly into the nitroso group, whereas in the course (b) one of the sulfonate oxygen is converted to the nitroso oxygen. The excess ^{18}O atom % in the nitrosomesitylene found can be explained if course (a) and (b) take place in the ratio of 1 : 2.

References

1) H.-J. Teuber and G. Jellinek, *Chem. Ber.*, **85**, 95 (1952).

2) M. Aoyama, T. Takahashi, H. Minato, and M. Kobayashi, *Chem. Lett.*, **1976**, 245.