Spectroscopic Investigation of Hydrocellulose Phenylosazones in Cadoxen Solution

H. S. BLAIR and R. CROMIE,* *Department of Chemistry (Industrial), Queen's University, Belfast, Northern Ireland*

Synopsis

Solutions of hydrocellulose phenylosazone in cadoxen are stable when oxygen is excluded. In the presence of oxygen, the absorption spectrum changes, but the change is partially reversible when nitrogen is bubbled through the oxidized solution. It is probable that a hydroperoxide of the hydrocellulose phenylosazone is formed initially and is then decomposed by the basic solvent. The work indicates the importance of using deoxygenated solvents and working in an oxygen-free atmosphere when preparing cadoxen solutions of hydrocellulose phenylosazone.

INTRODUCTION

Recently, the authors described the use of cadoxen solutions of cellulose phenylosazone for the spectroscopic determination of degradation and reported that these solutions underwent a change in absorbance with time,[1] but with the rigorous exclusion of oxygen the change was negligible. The present work describes a detailed investigation of this change.

EXPERIMENTAL

Hydrocellulose phenylosazones and cadoxen solutions were prepared as previously described.[1] Ultraviolet absorption spectra were determined using Unicam SP800 and Unicam SP500 spectrophotometers, and infrared absorption spectra were determined using a Unicam SP200.

RESULTS AND DISCUSSIONS

The absorption spectrum of a freshly prepared cadoxen solution of hydrocellulose phenylosazone is shown in Figure 1. The spectrum is characterized by maxima at 390 nm and 255 nm. The absorption spectrum changes appreciably in the presence of oxygen, as shown in Figure 2, the main features of the change being (i) a decrease in the intensity of the maximum at 390 nm (Fig. 3), (ii) the development of a new maximum at 277 nm whose intensity after some time slowly decreases (Fig. 4), and (iii) the presence of

* Present address: School of Physical Science, Ulster College, Northern Ireland Polytechnic, Jordanstown, Newtownabbey, Co. Antrim, Northern Ireland.
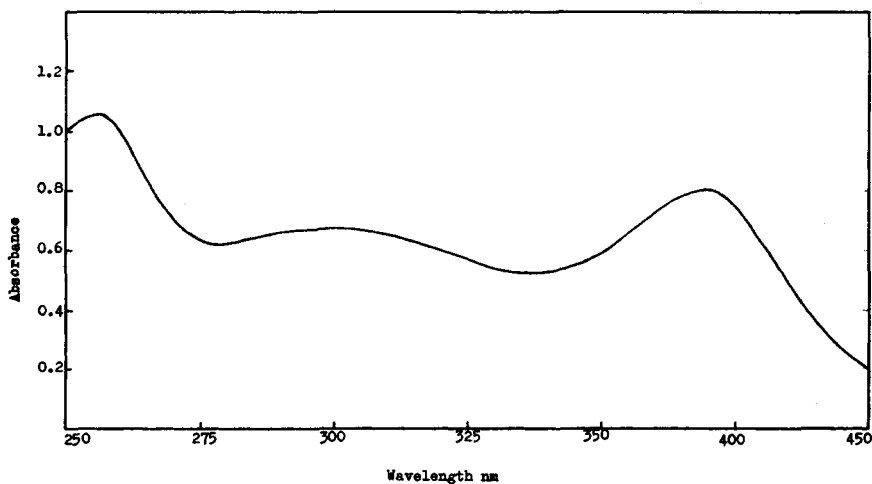
Fig. 1. Absorption spectrum of hydrocellulose phenylosazone in cadoxen solution.
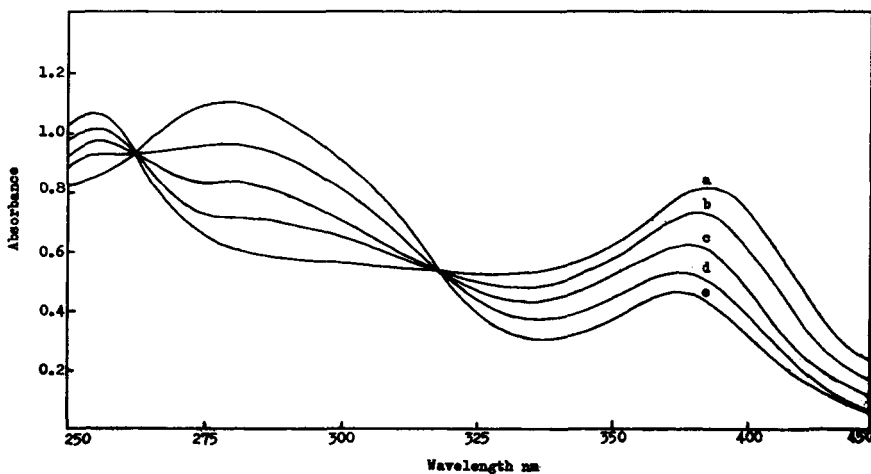

Fig. 2. Absorption spectrum of hydrocellulose phenylosazone in cadoxen solution: (a), freshly prepared; (b), (c), (d) and (e), after 10, 20, 30, and 40 min., respectively.

two sharp isosbestic points at 317 nm and 263 nm, which become less well defined after about 1 hr.

The cadoxen solutions of hydrocellulose phenylosazone obey Beer's law at 390 nm, and so absorbance values may be substituted for concentrations in the rate equation. The modified first-order rate equation of Guggenheim was used, as with this equation neither the initial nor the final absorbances need be known.[2] Absorbance measurements were made at constant time intervals Δ and were substituted in the Guggenheim equation giving

$$\log_{10} (A_t - A_{t+\Delta}) = -\frac{kt}{2.303} + a\ constant \qquad (1)$$
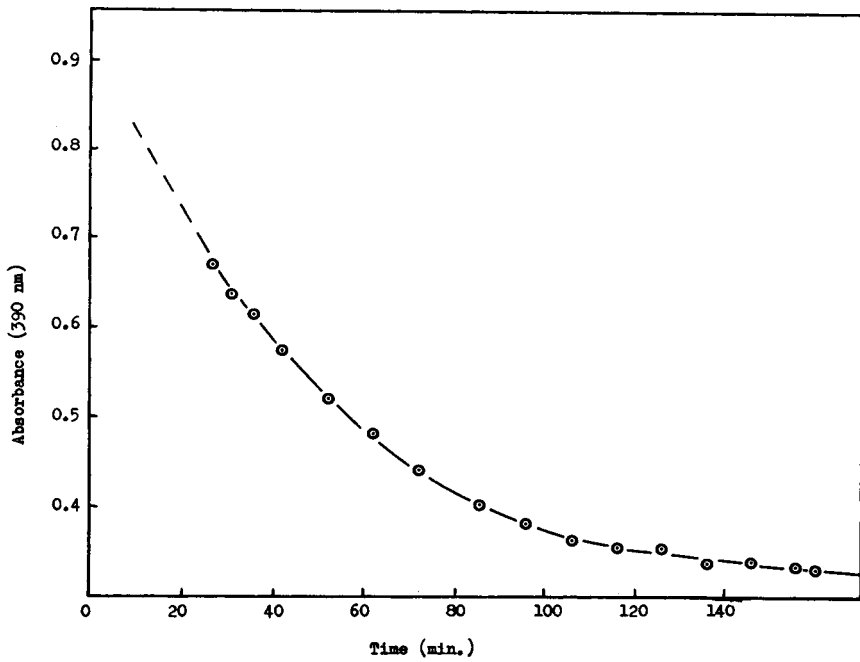
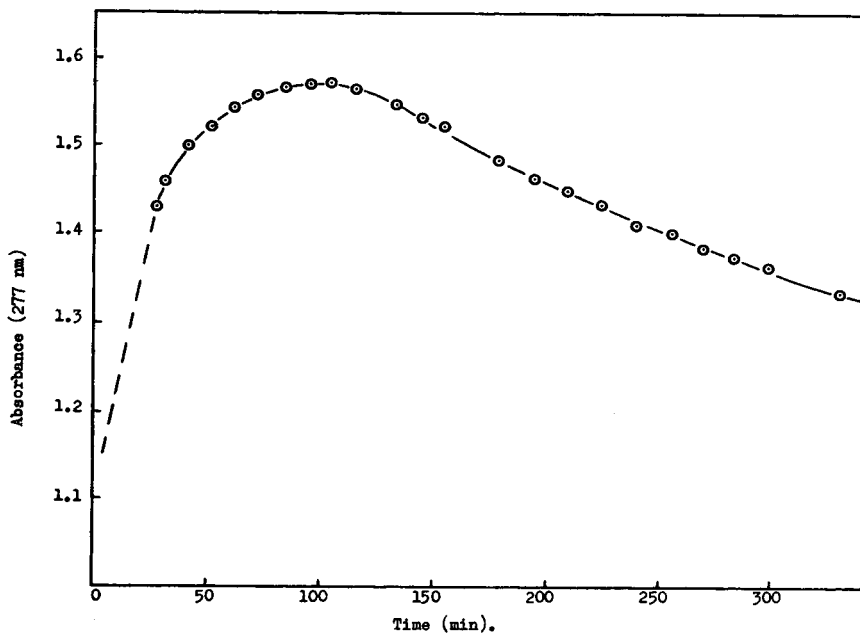Fig. 3. Change in absorbance of hydrocellulose phenylosazone at 390 nm.

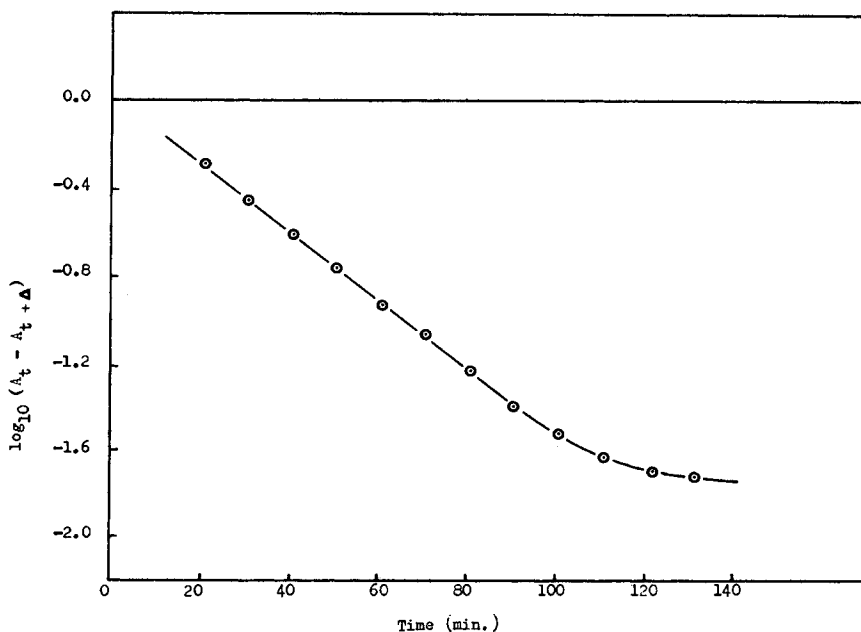Fig. 4. Change in absorbance of hydrocellulose phenylosazone at 277 nm.

Fig. 5. First-order reaction plot for hydrocellulose phenylosazone in cadoxen.

A plot of $\log_{10} (A_t - A_{t+\Delta})$ against t is shown in Figure 5. The plot is linear for the initial stages of the reactions; but as the reaction proceeds, the graph becomes nonlinear, indicating that first-order kinetics are no longer being followed.

Phenylosazones are unstable toward bases and are also oxidized by oxygen (or air) in alkaline solution.[3] Direct alkaline degradation of the phenylosazone would lead to "pseudo" first-order kinetics owing to the large excess of strongly alkaline solvent, whose concentration may be considered to be constant. The fact that the reaction kinetics do not remain first order throughout indicates that a more complex reaction scheme is involved. If the phenylosazone is being oxidized in cadoxen solution by oxygen dissolved in the solvent, then the observed kinetics may be explained by assuming that as the initial excess of oxygen is reduced, pseudofirst-order kinetics would no longer be observed.

To determine whether the degradation reaction was in fact oxidation of the osazone by dissolved oxygen, a sample of hydrocellulose phenylosazone was dissolved in 50% cadoxen and air was constantly passed through the solution. The absorption at 390 nm was determined at regular intervals, and using the results obtained, the values of $\log (A_t - A_{t+\Delta})$ were calculated. The resulting plot of $\log (A_t - A_{t+\Delta})$ versus time is linear over the complete time range studied and is shown in Figure 6. As a result, it may be concluded that the phenylosazones are oxidized in cadoxen solution resulting in a product which absorbs at 277 nm.
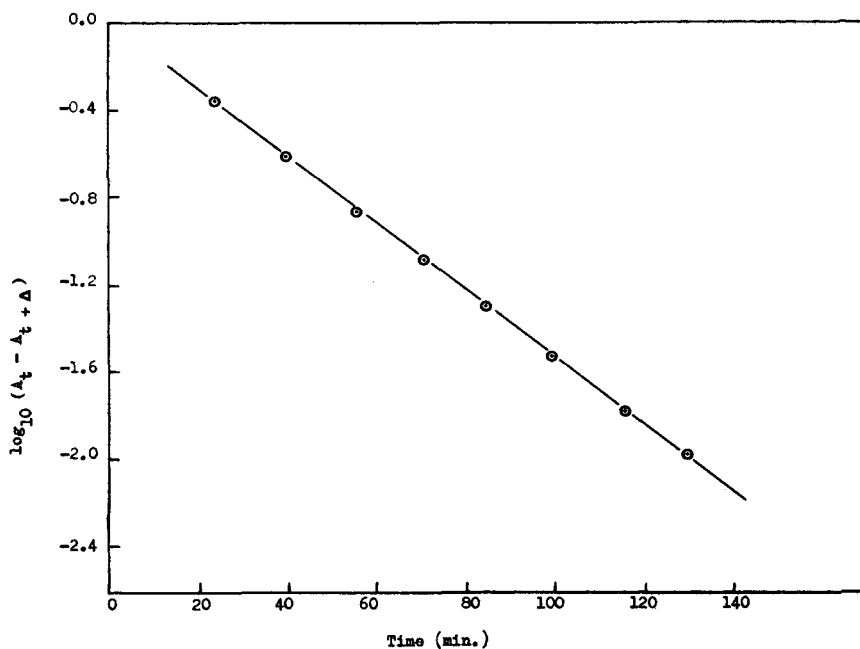
Fig. 6. First-order reaction plot for hydrocellulose phenylosazone in cadoxen with an excess of oxygen.

The fact that isosbestic points exist in the early stages of the reaction indicates that two absorbing species are present in the early stages. However, since the isosbestic points become indistinct as the reaction proceeds, there must be more than one reaction taking place, a fact which is also indicated by the eventual decrease in absorbance at 277 nm.

If we consider the general reaction scheme for consecutive reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$
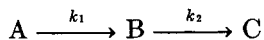
the rate equations describing this system are

$$\ln \frac{A_0}{A} = k_1 t \tag{2}$$

$$B = \frac{A_0 k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \tag{3}$$

Equations (2) and (3) give a complete kinetic description of the system, since $dA + dB + dC = 0$, where the terms have their usual significance.

In Figures 3 and 4, the absorbances of a cadoxen solution of hydrocellulose phenylosazone at 390 nm and 277 nm are plotted as a function of time.

The pattern of change is that predicted by a consecutive reaction scheme; it may be concluded that hydrocellulose phenylosazone is degraded in this manner, with $k_1 > k_2$:

$$A \xrightarrow[0]{k_1} B \xrightarrow{k_2} C$$
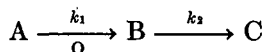
In an attempt to establish the nature of the second reaction, B → C, a hydrocellulose phenylosazone sample was dissolved in cadoxen, left for 30 min, and then precipitated, washed, dried, and redissolved in cadoxen. The absorption of the precipitated sample was the same as that of the original sample, with only a slight reduction in absorbance at 390 nm. However, when a sample was left in solution for 5 hr, precipitated, and redissolved, there was a large reduction in absorbance over the whole spectrum.

Due to the fact that the initial oxidation reaction is faster than the second reaction, there is a progressive buildup of the oxidation product B in solution. After 30 min, a relatively small amount of B will have reacted further to compound C. The fact that the absorption spectrum of the sample precipitated after 30 min in solution is almost identical to that of the original compound indicates that the initial reaction is reversed on precipitation. After 5 hr, a substantial amount of compound B will have reacted to give compound C, and the fact that the sample precipitated after 5 hr does not have similar absorption to the original sample indicates that the second reaction is not reversed on precipitation.

The infrared absorption spectrum of a low molecular weight hydrocellulose phenylosazone (high phenylosazone content) was determined. The spectrum exhibited a high-intensity absorption band at 1600 cm^{-1} due to the phenyl ring.

The infrared spectrum of the phenylosazone precipitated after 5 hr in solution was also determined, and a large reduction in the intensity of the 1600 cm^{-1} band was observed, indicating that the phenylosazone endgroup was being removed from the hydrocellulose molecule. Thus it was concluded that the second reaction is a cleavage reaction, probably a base-catalyzed hydrolysis of the phenylhydrazine residued from C_1 and/or C_2. As it was established that the degradation of hydrocellulose phenylosazone involves an initial oxidation, a sample of hydrocellulose phenylosazone was dissolved in cadoxen and the solution deoxygenated with oxygen-free nitrogen. It was found that the absorbance of the solution at 390 nm no longer decreased, but there was in fact a slight increase in absorbance. Thus, in addition to stopping the reaction, nitrogen appeared to reverse the reaction and convert the small amount of compound B formed during dissolution back to the original phenylosazone.

This reaction was studied further by passing air through a cadoxen solution of hydrocellulose phenylosazone at 25°C and removing samples at regular intervals for absorbance measurements. After 90 min, the air flow
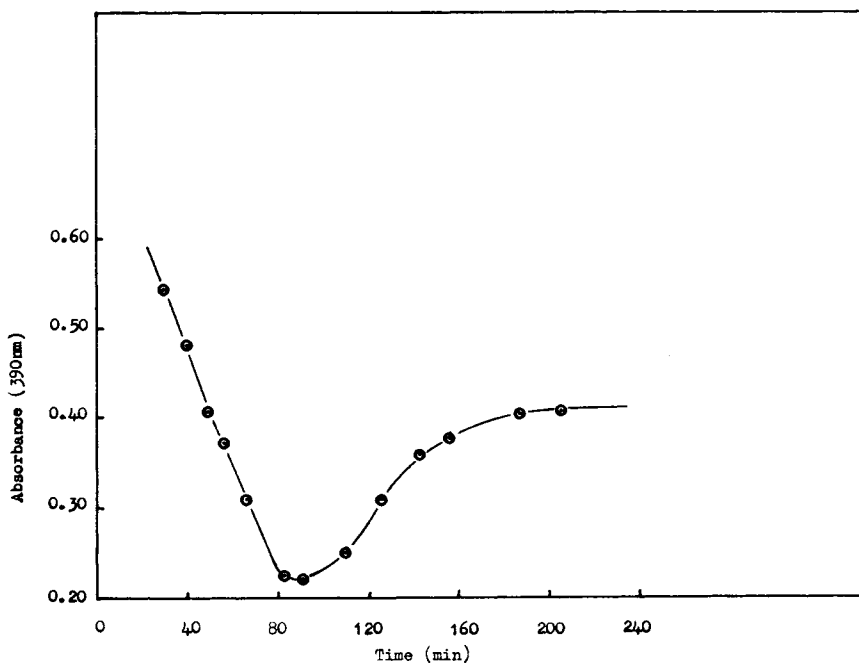
Fig. 7. Change in absorption of hydrocellulose phenylosazone at 390 nm under oxygen and nitrogen.
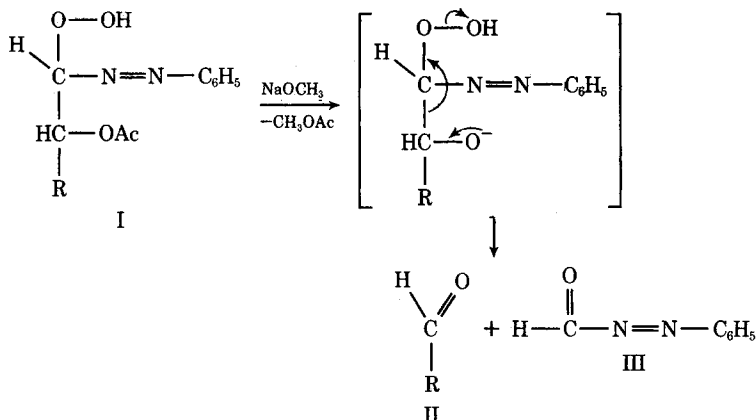
was switched off and nitrogen was passed through the solution. Absorbance measurements were again made on the solution at regular intervals, and the full results for the change in absorbance at 390 nm are shown in Figure 7. When air is passed through the solution, the absorbance at 390 nm decreases in the usual manner; but when the air flow is replaced by nitrogen the maximum at 390 nm increases in intensity.

However, the absorbance does not return to its original value but remains below it by an amount ΔA. If air is passed through the solution for longer periods before switching to nitrogen, ΔA is also increased. The fact that the absorbance does not return to its original value may be explained by the consecutive reaction mechanism proposed earlier, since a portion of the "oxidized" phenylosazone will have been converted irreversibly to compound C.

Nitrogen, which is chemically inert, is capable of reversing the initial reaction, and this suggests that the hydrocellulose phenylosazone is not in fact oxidized but rather forms an unstable "oxygenated complex" with oxygen and that the complex is decomposed when the oxygen concentration in the solution is reduced.

Buckingham and Guthrie[4] reported that 3,4,5,6-tetra-O-benzyl-D-glucose phenylhydrazone in dioxan solution on exposure to air forms the corresponding phenylhydrazine hydroperoxide. Schulz and Somoggi[5] ob-

tained the hydroperoxide I on passing oxygen through a benzene solution of penta-O-acetyl-D-galactose phenylhydrazone. This hydroperoxide on treatment with sodium methoxide decomposes giving a sugar with one carbon atom less, D-lyxose (II), and probably N-formyl-N'-phenyldiazine (III). The mechanism proposed by Schulz and Somoggi for this decomposition is shown below:

$$
\begin{array}{c}
\text{O——OH} \\
\text{H}\diagdown\ \ | \\
\quad\ \text{C—N}\!\!=\!\!\text{N—C}_6\text{H}_5 \\
\quad\ | \\
\text{HC——OAc} \\
\quad\ | \\
\quad\ \text{R} \\
\qquad \text{I}
\end{array}
\xrightarrow[\text{—CH}_3\text{OAc}]{\text{NaOCH}_3}
\left[
\begin{array}{c}
\text{O}\overset{\frown}{}\text{OH} \\
\text{H}\diagdown\ \ | \\
\quad\ \text{C}\!\!-\!\!\text{N}\!\!=\!\!\text{N—C}_6\text{H}_5 \\
\quad\ | \\
\text{HC}\overset{\frown}{}\text{O}^- \\
\quad\ | \\
\quad\ \text{R}
\end{array}
\right]
$$

$$
\Big\downarrow
$$

$$
\begin{array}{c}
\text{H}\diagdown\ \ \text{O} \\
\quad\ \text{C}\!\!\diagup\!\!/ \quad + \quad \text{H—C—N}\!\!=\!\!\text{N—C}_6\text{H}_5 \\
\quad\ | \qquad\qquad\qquad\ \ \text{III} \\
\quad\ \text{R} \\
\quad\ \text{II}
\end{array}
$$

In the decomposition of hydrocellulose phenylosazone, it is probable that a hydroperoxide is formed which is then decomposed by the basic solvent, resulting in scission of the phenylhydrazine residue from the hydrocellulose. The C_2 phenyldrazine is hydrolyzed first since it is more susceptible to hydrolysis[6] than that on C_1:

$$
\begin{array}{c}
\text{O——OH} \\
\quad | \\
\text{HC——N}\!\!=\!\!\text{N—C}_6\text{H}_5 \\
\quad | \\
\text{HC}\!\!=\!\!\text{N—NH—C}_6\text{H}_5 \\
\quad | \\
\quad \text{R}
\end{array}
\xrightarrow[\text{OH}^-]{\text{H}_2\text{O}}
\left[
\begin{array}{c}
\text{O}\overset{\frown}{}\text{OH} \\
\quad | \\
\text{HC}\!\!-\!\!\text{N}\!\!=\!\!\text{N—C}_6\text{H}_5 \\
\quad | \\
\text{HC}\overset{\frown}{}\text{O}^- \\
\quad | \\
\quad \text{R}
\end{array}
\right] + \text{H}_2\text{N—NH—C}_6\text{H}_5
$$

hydrocellulose phenylosazone
hydroperoxide

$$
\Big\downarrow
$$

$$
\begin{array}{c}
\text{H}\diagdown\ \ \text{O} \\
\quad\ \text{C}\!\!\diagup\!\!/ \quad + \quad \text{H—C—N}\!\!=\!\!\text{N—C}_6\text{H}_5 \\
\quad\ | \\
\quad\ \text{R}
\end{array}
$$
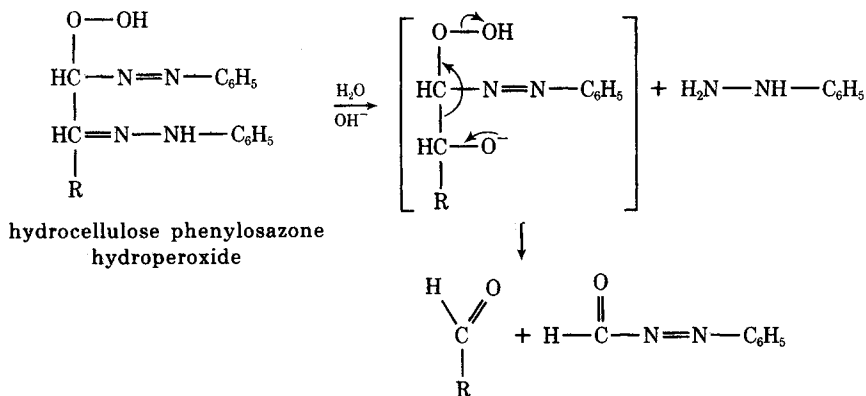
CONCLUSIONS

While a cadoxen solution of hydrocellulose phenylosazone is stable when kept free from oxygen, the work described above indicates the importance of using deoxygenated solvents and working in an oxygen-free atmosphere when preparing these solutions.

References

1. H. S. Blair and R. Cromie, *J. Appl. Polym. Sci.*, **16,** 3063 (1972).
2. A. E. Guggenheim, *Phil. Mag.*, **2,** 538 (1926).
3. O. Diels, R. Meyers, and O. Onnen, *Ann.*, **525,** 94 (1936); O. Diels, O. Cluss, H. J. Stephan, and R. König, *Ber.*, **71,** 1189 (1938).
4. J. Buckingham and R. D. Guthrie, *J. Chem. Soc.* (C), 2268 (1967).
5. M. Schulz and L. Somoggi, *Angew. Chem. Int. Ed.*, **6,** 168 (1967).
6. G. Henseke, *Acta Chim. Acad. Sci. Hung.*, **12,** 173 (1957).