ANODIC OXIDATION OF HYDRAZINE ON SILVER

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Abstract. The oxidation of hydrazine in alkaline solutions was investigated on silver electrode. Coulometry, potentiostatic pulse and sweep methods were employed to investigate the reaction. The results show that the overall reaction involves four electrons and that the rate of reaction is limited by 1 e transfer in the first step. The reaction was found to be first order with respect to hydrazine and independent of hydroxyl ion concentration in the range, investigated.

Hydrazine is now well known for it's use in fuel cell. Over the past decade, many research workers have attempted to investigate the mechanism of it's oxidation in various solutions and at various electrodes. The conclusions of various workers on Hg electrode are in agreement[1-3]. The results on Pt electrode are not in agreement[1,3-10]. Some work has also been reported on Ni,[11-14] platinized/palladized carbon,[15-17] carbon[18] and gold[2,19] electrodes. On silver, the only work that has so far appeared in the literature is that of Korinek et al.[2] who used rotating disc technique to investigate the reaction.

The purpose of the present work was to investigate the oxidation of hydrazine in alkaline solution, using potential pulse and sweep methods. Coulometry was also performed to obtain the value of n and to see the character of the reaction.

Theoretical. Linear potential sweep and square potential pulse were used to investigate the reaction. The relevant theoretical treatment of these techniques is given in the literature.[20,25] The main advantage of these techniques is that the time of measurements is small (viz. a few msec) and thus one avoids the complications arising from the accumulation of products near the electrode.

In the case of an irreversible reaction (as in the present case), the pulse results (i—t transients) may be used to obtain Tafel plots (i—E curves when the current is not diffusion limited). This is done by utilizing the pulse results at low over-potentials, when the i—t transients are flat (showing electrochemical control). The i—t curves (showing partial diffusion control) may also be used by extrapolating out the diffusion.[25] The number of electrons involved in the overall reaction(n) can be found from the limiting i—t curves for which the equation is as follows:[24,25]

$$i = nFAD^{\frac{1}{2}}C \frac{1}{(\pi t)^{\frac{1}{2}}} \tag{1}$$

where A is electrode area, D and C are diffusion coefficient and concentration of the reactant respectively.

Similarly the sweep results of an irreversible reaction may be analysed by the following equations:[23,24]

$$i_p = 0.496\, n\, FACD^{\frac{1}{2}} \left(\frac{\alpha n_a E \nu}{RT} \right)^{\frac{1}{2}} \tag{2}$$

$$E_p = E_i + \frac{RT}{\alpha\, n_a} \left\{ -0.78 + \ln(k/D^{\frac{1}{2}}) - \tfrac{1}{2}\ln\left(\frac{\alpha n_a E \nu}{RT} \right) \right\} \tag{3}$$

where i_p and E_p are peak current and peak potential respectively. ν is sweep rate, α is the charge transfer coefficient and n_a is the number of electrons involved in the first and the rate determining step. E_i (initial potential) is that potential above which the reaction becomes diffusion limited. αn_a values may be calculated from the plots of i_p—$\nu^{\frac{1}{2}}$ and E_p—$\log \nu$ by using equations 2 and 3 respectively.

It may be mentioned that the diffusion of only one species (reactant) has been considered in deriving equations 2 and 3. So far, no equations have been derived to account for the diffusion of more than one species. However, the problem is solved by taking a much smaller concentration of the reactant as compared to that of reaction partner. Under such conditions the current will be controlled only by the diffusion of the reactant. It is obvious that in such a case, i_p will be given by equation 2. However, though the relation between E_p and ν will still be given by equation 3, but the actual values of E_p will change with the change in concentration of the reaction partner, provided the reaction partner affects the rate of reaction. The dependence of E_p on the concentration of reaction partner is obvious from the fact that E_p is related to E_i (equation 3). Thus any shift in E_i will produce a corresponding shift in E_p. The E_i shift will be the same as the shift of Tafel plots along the potential axis.

Experimental

Instruments and Cells. A potentiostat (Chemical Electronics Co. model TR 70/2A) and a function generator (Chemical Electronics Co., type RB1) were used to apply desired potential profile to the working electrode. Pulse and sweep results were displayed on an oscilloscope (Tetronix type 503) which were recorded photographically. The results of coulometry were recorded on a chart-recorder.

The pulse/sweep experiments were carried out in the glass cell shown in Fig. 1. A luggin capillary

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Notations: i, current; i_p, peak current; E_p, peak potential; ν, sweep rate; α, charge transfer coefficient; n, number of electrons involved in the overall reaction; n_a, number of electrons involved in the rate determining step.

(not shown) entered the cell through a socket (dotted circle in Fig. 1). The luggin capillary was connected to the reference electrode compartment at the other end. The liquid junction was made at the three-way tap connecting the reference compartment and the luggin capillary.

The cell for coulometry was similar to that shown in Fig. 1 except that the working and the counter electrodes entered the cell from opposite ends through B_{29} sockets.

Reference Electrodes. $Hg/HgO/OH^-$ system was used as the reference electrode. At least three reference electrodes were prepared (for any concentration of OH^-) for comparison against one another and were stored in a four-armed container. The electrodes matched one another to within 0.1 mV.

Working and Counter Electrodes. The pulse/sweep experiments were affected on a sphere produced by melting one end of a pure silver wire and sealing the Ag-sphere in the sliding joint of a glass syringe with Araldite (Fig. 1). Due to the possible presence of oxides on the surface of Ag-sphere, the electrode was electropolished in a solution consisting 30 g AgCN, 30 g KCN and 38 g K_2CO_3, all dissolved in 1 litre distilled water. The electropolishing was done in a simple H-shaped cell, employing a silver-coated Pt-sphere as the reference and a Pt-gauze as the counter electrode. To start with, the electropolishing was done for about 20 min at $+0.6$ V vs the reference electrode. Due to this treatment, the electrode became smooth and shiny. The electropolishing was also done for 20–30 sec before running various experiments as will be described later. The area of Ag-sphere, as measured microscopically, was 0.074 cm².

The working electrode for coulometry consisted of Ag-wire wound into a spiral and sealed in a B_{29} cone. The electropolishing was not necessary for this electrode, however, the electrode was polarised cathodically (at about -0.5 V vs Hg/HgO) in NaOH solution prior to making a coulometric run.

Purification and Cleaning. Mercury, used in reference electrodes, was purified by double vaccum distillation. Analar hydrazine sulphate (used in making solutions) was further purified by recrystallization from triply distilled water. Base solutions, made from Analar NaOH, were further purified by pre-electrolysis.

All glassware was cleaned with chromic–sulphuric mixture and then thoroughly flushed with triply distilled water.

Measurements. All solutions were deoxygenated by bubbling N_2 prior to making a run. In case of pulse/sweep, nitrogen was forced at the electrode to remove N_2 bubbles sticking to the electrode before each
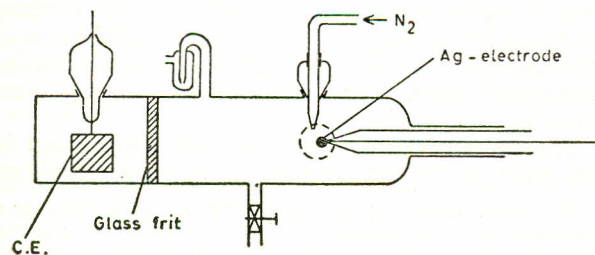
measurement. The solution was allowed to be quiescent for 45 sec before applying pulse/sweep.

In case of coulometry N_2 was left bubbling in the solution at a fixed rate throughout the run. The coulometric graph was recorded till the current fell below 0.1 mA.

Results and Discussion

Coulometry. Coulometry was performed on 5 mM hydrazine solutions in 1M and 0.1M NaOH at two different potentials for each solution. The coulometric curves and the corresponding log i—t curves for hydrazine in 1M NaOH solution are shown in Figs 2 and 3. Results in 0.1M NaOH were similar to those in Figs. 2 and 3.

Calculation of charges under the curves of Fig. 2 showed $n = 4$ in each case. This also shows that the overall reaction is potential-independent. Fig. 3 shows that the oxidation is not complicated by the intermediate products. The straightforward conclusion, as observed by other workers on many other metals, is that the overall reaction is as follows:
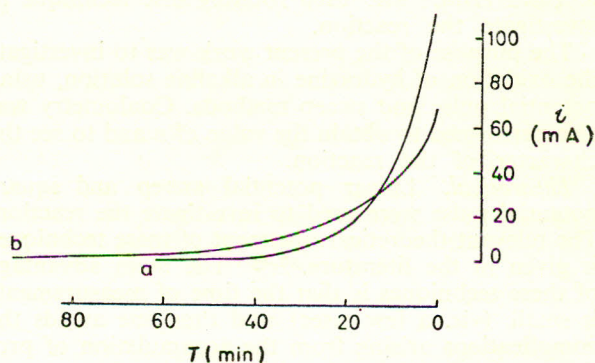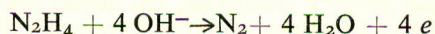
$$N_2H_4 + 4\,OH^- \rightarrow N_2 + 4\,H_2O + 4\,e$$

Fig. 2. Coulometric curves for 5mM hydrazine in 1M NaOH at fixed potentials: a, 0.05 V; b, 0.25 V vs Hg/HgO/NaOH (0.1M).

Fig. 3. i—t plots from Fig. 2.
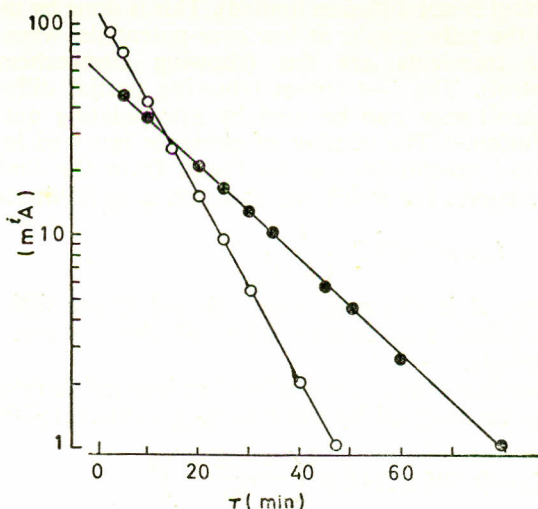

Fig. 1. Cell for electrochemical measurements.

Potentiostatic Pulse and Sweep. The standing potentials were chosen between — 0.5 V to — 0.6 V vs Hg/HgO. There was no current in the cell at these potentials, for the solutions investigated. More negative potentials were avoided for fear of depositing sodium layer on the electrode.[26]

Before we present the results, a few preliminary observations may be mentioned. It was observed that the activity of the electrode went down with lapse of time. This was clearly due to adsorption of impurities on the electrode from the solution. However, with a freshly electropolished electrode the results were reproducible for $\frac{1}{2}$ to 1 hr. Thus, the measurements, in a given solution, were made within this time and the electrode was freshly polished before use in any solution. However, even when the electrode was polished before each run, an unreproducibility up to ±20 mV (viz for *i—E* curves) was observed. This is due to the fact that electropolishing does not reproduce the electrode surface exactly.

A typical limiting *i—t* transient is shown in Fig. 4. From such curves, the *i—t$^{\frac{1}{2}}$* plots for two different concentrations of hydrazine are shown in Fig. 5. The value $n = 4$ was obtained from *i—t$^{\frac{1}{2}}$* plots (Fig. 5) according to equation 1. This result is in agreement with the coulometric result.
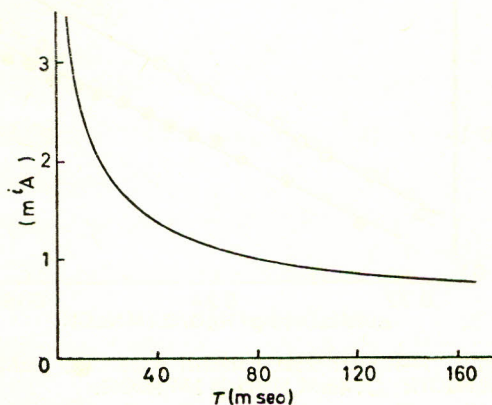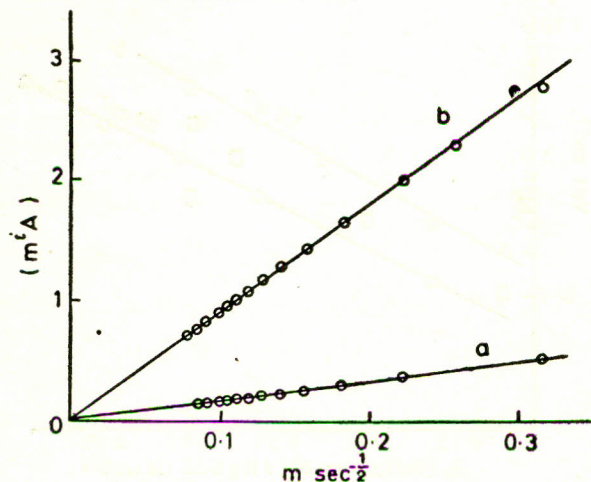
Now, to find the value of αn_a and the reaction order with respect to hydrazine, consider the following results.

Using a freshly electropolished electrode, 1 and 5 mM hydrazine in 1M NaOH solution were studied in succession. The Tafel plots, obtained from pulse *i—t* transients, for these solutions are shown in Fig 6. The current rise in going from 1 to 5mM in Fig. 6 gives an exactly first order with respect to hydrazine. However, when the same electrode was used in another solution of hydrazine, the Tafel plot was found to be slightly out of the expected place in Fig. 6. The reason for this has already been described.

Thus results were obtained in various solutions by using a freshly polished electrode in each case. It may be mentioned that in cases when the concentration of NaOH in the reference electrode was different from that in the working solution, the results were corrected for liquid junction potential by use of Henderson's equation.

The current at fixed potential for various concentrations of hydrazine is shown in Fig. 7. The two points at 2 mM hydrazine concentration show the unreproducibility observed. Fig. 7 shows clearly that the reaction is first order in hydrazine. The Tafel slopes were found to be 110–120 mV (as in Fig. 6) in all cases. These Tafel slopes show that the oxidation involves one electron in the first step which is also the rate determining step.

In the sweep results, the i_p was found to be strictly proportional to hydrazine concentration. i_p vs $v^{\frac{1}{2}}$ plots for various concentrations of hydrazine in 1M NaOH are shown in Fig. 8. Calculations according to equation 2 gave $\alpha n_a = 0.5$ from each plot in Fig. 8.

To see the order of reaction with respect to OH⁻, the effect of varying the OH⁻ concentration was studied on *i—E* and E_p—log v plots. Consider the following set of experiments—

After electropolishing the electrode for 20 sec, pulse and sweep measurements were made in a 4 mM

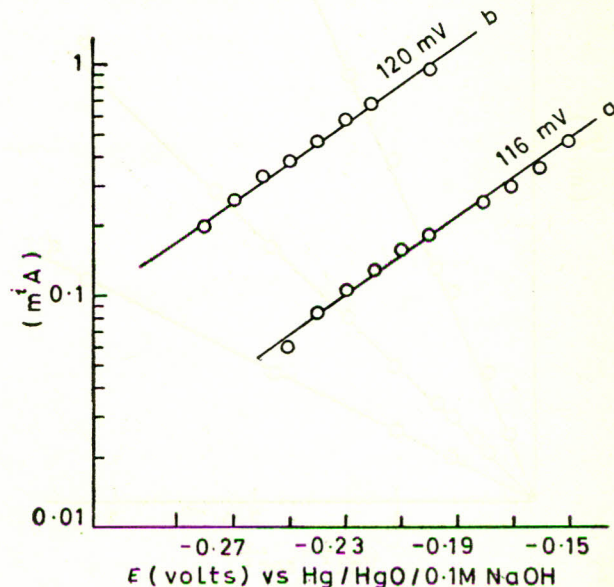Fig. 4. Limiting *i—t* transients for 5mM N₂H₄ in 1M NaOH at —40 mV vs Hg/HgO/NaOH (0.1M).

Fig. 5. *i—t$^{\frac{1}{2}}$* plots from limiting *i—t* transients in N₂H₄, 1M NaOH solution: a, 1mM; b, 5mM N₂H₄.

Fig. 6. *i—E* plots from potential pulse: a, 1mM N₂H₄ in 1M NaOH; b, 5mM N₂H₄ in 1M NaOH.
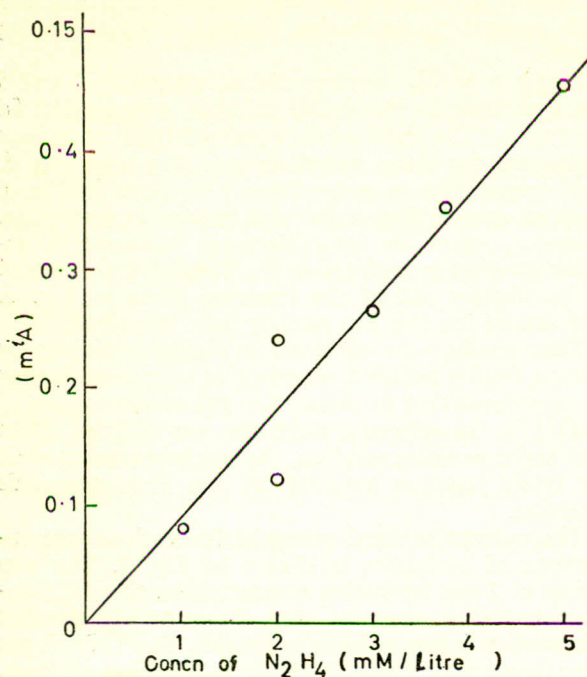
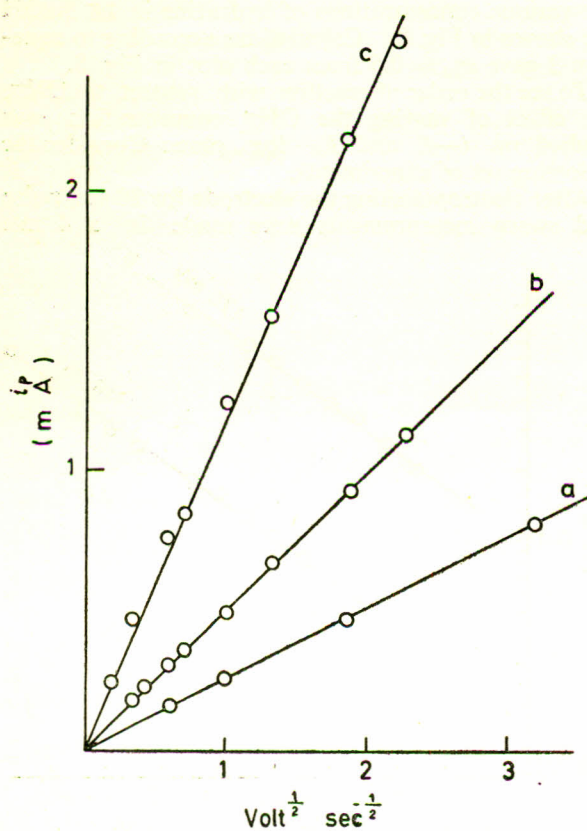Fig. 7. i—N_2H_4 (concd) at fixed potential (—0.25 V vs Hg/HgO/0.1 M NaOH).

hydrazine (0.1 M NaOH) solution. The Tafel plot and the E_p—log ν curves thus obtained are shown by curves 'a' in Figs. 9 and 10. The electrode was polished again for 15 sec and then used in 4 mM hydrazine (1 M NaOH) solution. The E_p values thus obtained fell very close to curve 'a' in Fig. 10. The point ($\square$) below the curve 'a' shows deactivation of the electrode observed after sometime after the measurements had been made. The i—E curve for this solution (not shown) also fell close to curve 'a' in Fig. 9. After these measurements, the electrode was electropolished again for 15 sec and used in the same 4 mM hydrazine (1 M NaOH) solution. The results thus obtained are shown by curves 'b' in Figs 9 and 10. Similar results were obtained in other set of experiments when the concentration of NaOH was varied from 1 M to 0.02 M,

   The results clearly indicate that the reaction does not involve OH^- in the rate determining step. If OH^- was involved even to the first order, one would expect a cathodic shift of about 120 mV in the Tafel plots for a ten-fold increase of OH^- concentration. A similar shift would be observed for E_p—log ν plots. The observed cathodic shift of Tafel plots and E_p—log ν plots in Figs. 9 and 10 is too small to account for the de-
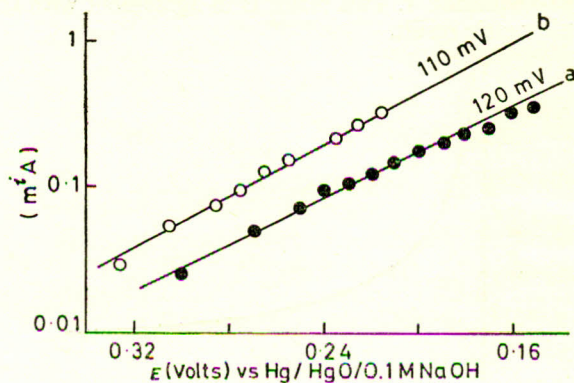

Fig. 9. i—E plots from potential pulse. ●, 4mM N_2H_4 in 0.1 M NaOH; ○, 4mM N_2H_4 in 1 M NaOH.

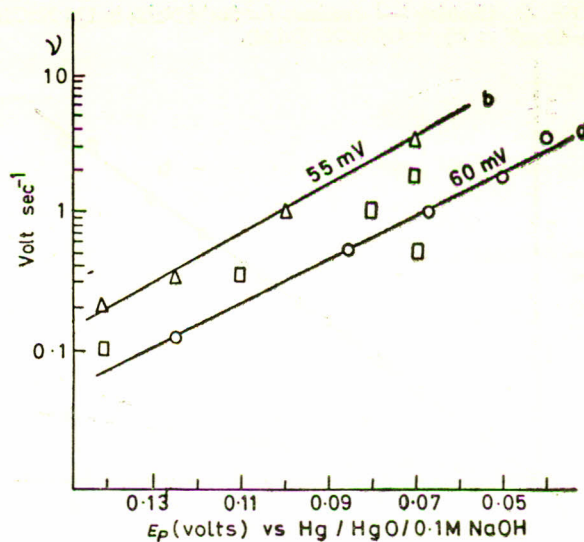Fig. 8.   Dependence of peak current on sweep rate in 1 M NaOH solution: a, 1mM; b, 2mM; c, 5mM N_2H_4.

Fig. 10. E_p—ν curves.   O, 4mM N_2H_4 in 0.1 M NaOH;   □ and △ 4mM N_2H_4 in 1 M NaOH.

pendence of reaction rate on OH⁻, even to the first order. The shifts in Figs. 9 and 10 are only due to electropolishing before each run, which, as already described, does not reproduce exactly the condition of electrode surface.

Finally, an interesting observation may be mentioned. It was observed that in sweep experiments, if the cathodic (initial) limit was chosen as about —1.0 V (vs Hg/HgO), the E_p values were found to lie more cathodic than when the initial potential was chosen as about —0.5 V. A similar effect was observed for the Tafel plots. This phenomenon is similar to that observed by Korinek et al.[2] in their i—E curves obtained by rotating disc experiments. However, their interpretation of this observation[2] based on the removal of oxides (of Ag) at more negative potentials, is in error. Even if oxides were present on Ag-electrode to start with, they would quickly reduce at a potential cathodic to the thermodynamic potentials for such oxides. For example, the thermodynamic potential for Ag/Ag_2O is about +0.24V vs Hg/HgO electrode. Thus the oxides would not exist at the potentials where the hydrazine reaction has been studied. The most probable explanation of the observed shift of E_p (or $E^{\frac{1}{2}}$ of Korinek et al.[2]) would be in terms of the reported deposition of sodium ions on silver at much negative potentials.[26] This would mean that the rate of reaction is faster on sodiun-coated Ag than on bare silver.

Conclusion

The experimental results show that 4 e are involved in the overall reaction and that 1 e is involved in the first and the rate determining step. The reaction is first order in hydrazine and is independent of OH⁻.

All the facts lead to the following mechanism.

$$N_2H_4 \xrightarrow{\text{Slow}} N_2H_4^+ + e \qquad (5)$$

$$N_2H_4^+ + 4OH^- \xrightarrow{\text{Fast}} N_2 + 4H_2O + 3e \qquad (6)$$
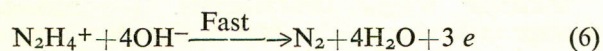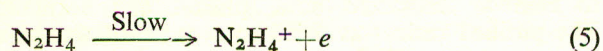
It is not possible to specify the mechanism any further as the steps, if any, contained in equation 6 are so fast that no intermediates could be detected.

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