

Semiconductor Electrodes

XXVIII. Rotating Ring-Disk Electrode Studies of Photo-oxidation of Acetate and Iodide at n-TiO₂

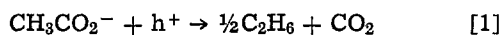
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ABSTRACT

The photo-Kolbe reaction (electro-oxidation of acetate) on TiO₂ in aqueous solution has been studied by means of a rotating ring-disk electrode (RRDE) with a TiO₂ disk and Pt ring. The oxidation of acetate competes very efficiently with water for photogenerated holes on the illuminated n-TiO₂ disk as shown by a decrease in the collection efficiency for oxygen reduction. No oxidation product of acetate was detected on the ring. Competitive oxidation of iodide with acetate and water was also investigated. Equations for determining relative rate constants for competitive reactions are derived and the applicability of the RRDE in studying such systems discussed.

Since the initial studies of the photo-oxidation of water at n-type TiO₂ (rutile) electrodes by Fujishima and Honda (1), investigations of this and many other reactions on this material have been reported. For example, the oxidation of many other substances (e.g., iodide, bromide, and cyanide ions) can be carried out at n-TiO₂ in competition with water oxidation (2, 3). Of particular recent interest has been the photo-Kolbe reaction in which a carboxylic acid is photo-oxidized (4, 5). For example, previous studies from this laboratory have established that in aqueous solutions containing acetate (Ac⁻)/acetic acid (HAc) mixtures irradiation of an n-TiO₂ electrode leads almost exclusively to the oxidation of acetate



(where h^+ represents a hole photogenerated at the TiO₂ surface). Photocatalytic decomposition of acetate (predominantly to methane and CO₂) has also been carried out by irradiation of suspensions of platinized TiO₂ (6, 7). While total product yields and current-potential (i - E) curves have yielded information about the overall course of the reaction (5) and electron spin resonance spin trapping experiments have established the intermediacy of methyl radicals in the reaction (8), studies of the relative rates of acetate vs. water oxidation have not been reported.

We describe here an investigation of acetate oxidation at a TiO₂-disk Pt-ring rotating ring-disk electrode (RRDE). In this research, products generated by photo-oxidation at the n-TiO₂ disk are swept to the Pt ring where they are detected. Relative values of the disk current (i_D) and the ring current (i_R) are then employed to obtain information on reaction rates. Previous photoelectrochemical studies employing the RRDE have proven very useful in elucidating reaction paths, relative reaction rates, and semiconductor stability (2, 9-13). In work closely related to that reported here, a TiO₂ disk RRDE was employed to study photo-oxidation of halide ions and reducing agents (2, 9).

Experimental

Chemicals.—Sodium sulfate, sodium acetate, glacial acetic acid (Fisher Scientific Company), and sodium iodide (Mallinckrodt Chemical Works) were of reagent grade. Triply distilled water was used as a solvent.

Apparatus and procedure.—A Tascussel Electronique Bipotentiostat, Model Bipad 2, was used for all experiments. A Wavetek function generator provided a

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d-c potential ramp for voltammetric experiments recorded on a Mosley Model 7005A X-Y recorder.

The construction of the RRDE generally followed that described by Fujishima *et al.* (9). The TiO₂ disk electrode was a single crystal, which was prepared by cutting a 1 mm thick slice, 5.5 mm in diameter, from a large single crystal (Fuji Titanium, Japan). This piece was reduced at 750°C under hydrogen for 30 min. The TiO₂ disk and Pt ring electrodes were mounted in a Teflon rod. On the back side of the TiO₂ disk an ohmic contact was made with Ga-In alloy to which a Cu-wire was attached with conducting silver epoxy. The Cu-wire was connected to a brass shaft. The platinum ring electrode had an inner radius (r_2) of 3 mm and an outer radius (r_3) of 6.25 mm. The collection efficiency for this electrode, N_o , defined as $-i_R/i_D$ for a stable system, was calculated to be 0.648 from the geometry (14). The measured value of N_o , determined by reduction of ferricyanide at the TiO₂ in the dark and oxidation of the resulting ferrocyanide at the Pt ring, was 0.65. The electrode was rotated with a Motomatic Model E-550 motor and controller (Electrocraft Corporation, Hopkins, Minnesota). Electrical contact to the shaft was made using two sets of silver graphite brush and leaf assemblies.

A saturated calomel electrode (SCE) was used as a reference and platinum foil served as the counter-electrode. The electrochemical cell had a 4 cm diameter and was 4.5 cm high; a glass basket inside prevented vortex formation at high rotation rates (15). The TiO₂ disk was irradiated through the cell bottom by the focused beam of a 400W xenon lamp. In all experiments, the solution was purged with nitrogen gas for more than 30 min before measurements.

Results

Acetate-free solutions.—The irradiation of the TiO₂ disk electrode immersed in 0.2M Na₂SO₄ solutions produces an anodic disk current and a flux of O₂ and some H₂O₂ to the ring electrode (Fig. 1, curve A) (1, 2, 16). The products are reduced at the ring electrode (Fig. 2, curve A). The ring current, attributed to oxygen (and H₂O₂) reduction, was very dependent upon solution purity. It is well known, see, e.g., Ref. (17), that oxygen reduction at a platinum electrode depends critically on the nature of the electrode surface and the presence of adsorbed impurities. To obtain reproducible ring currents for oxygen reduction, the ring electrode was cycled repeatedly between potentials for hydrogen and oxygen evolution just before the measurement of i_R (17, 18). With this procedure the value of i_R at $-0.2V$ vs. SCE divided by the disk photocurrent resulted in a collection efficiency of 0.63

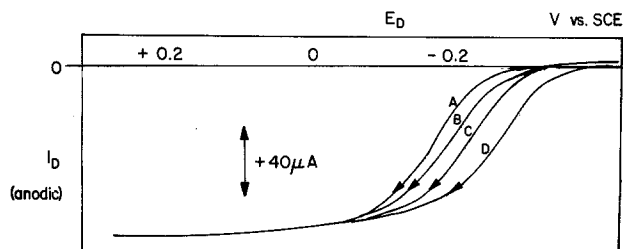


Fig. 1. Current-potential curves for an illuminated $n\text{-TiO}_2$ disk electrode in $0.2\text{M Na}_2\text{SO}_4$. (Curve A) no acetate; (curve B) 1 mM acetate; (curve C) 10 mM acetate; (curve D) 0.14M acetate; (curve E) in the dark. Rotation rate = 700 rpm ; potential scan rate, 22 mV/sec ; $[\text{NaAc}]/[\text{HAc}] = 1$.

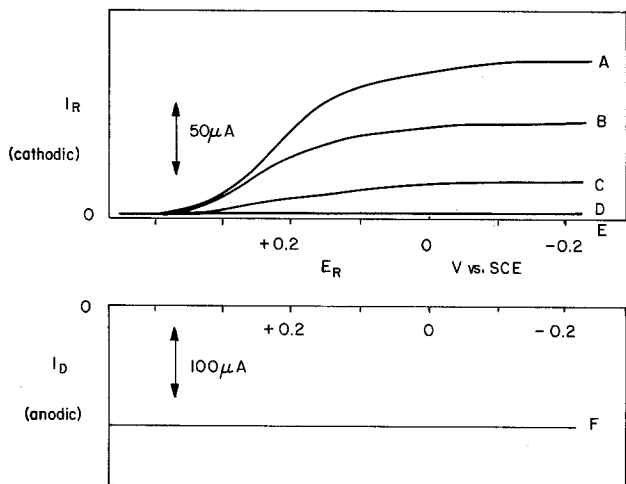


Fig. 2. Current-potential curves for Pt-ring electrode with illuminated $n\text{-TiO}_2$ disk electrode in $0.2\text{M Na}_2\text{SO}_4$. (Curve A) no acetate; (curve B) 0.03M acetate; (curve C) 0.14M acetate; (curve D) in the dark; (curve E) disk current in the dark (along X-axis); (curve F) disk current under illumination. $E_D = 1.0\text{V vs. SCE}$. Rotation rate, 700 rpm ; potential scan rate, 22 mV/sec . $[\text{NaAc}]/[\text{HAc}] = 1$.

which is quite close to the theoretical and experimental N_o -value (0.65).

Acetate-containing solutions.—The effect of addition of equimolar mixtures of sodium acetate and acetic

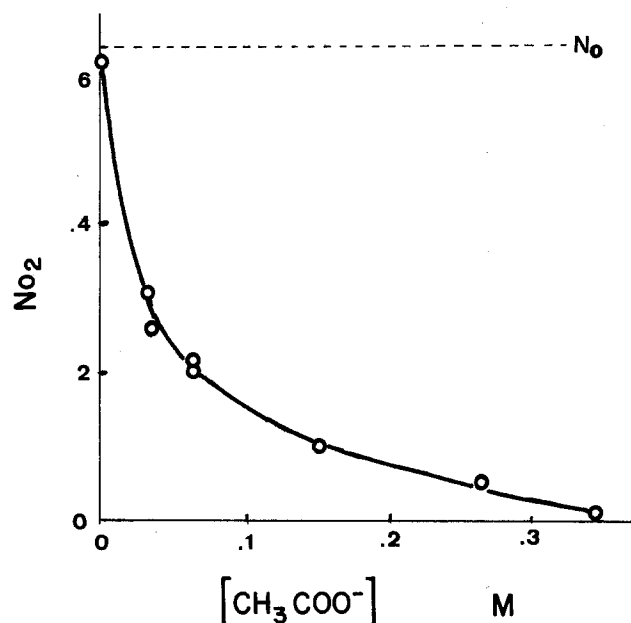


Fig. 3. Dependence of the collection efficiency for oxygen on the concentration of acetate. Rotation rate, 700 rpm ; $E_D = 1.0\text{V vs. SCE}$; $E_R = -0.2\text{V vs. SCE}$. $[\text{NaAc}]/[\text{HAc}] = 1$.

acid to the $0.2\text{M Na}_2\text{SO}_4$ solution ($\text{pH} = 4.7$) on the disk photocurrent at TiO_2 and the Pt ring current is shown in Fig. 1 and 2. The potential for the onset of the anodic photocurrent at TiO_2 shifts towards more negative values with the addition of acetate (Fig. 1, curves B-D), as found in a previous study (5). The limiting anodic disk current was unchanged by addition of acetate or rotation rate, demonstrating that this current was governed by the rate of generation of holes by light absorption and their flux to the electrode surface. The ring current was reduced by the addition of acetate (Fig. 2, curves B-C). The shape of the i_R - E_R curves was unchanged however by the addition of acetate and no new waves appeared. This demonstrates that the effect of acetate is to compete with water oxidation. Addition of acetate to an oxygen-saturated solution does not affect the limiting current for oxygen reduction at a platinum electrode, so that this decrease cannot be ascribed to this source. No product from the oxidation of acetate at the disk can be detected at the ring. This is in line with expectations, since the acetoxy radical produced by the initial oxidation step decomposes very rapidly to $\text{CH}_3\cdot$ and CO_2 . The methyl radicals rapidly react to form ethane and neither this species nor CO_2 is reducible at these potentials. Thus the ring current in acetate-containing solutions can only be ascribed to the reduction of products from the oxidation of water that competes with acetate for the photogenerated holes at the TiO_2 disk surface. We might note that the reduction of oxygen occurs on an $n\text{-TiO}_2$ electrode at potentials positive to the flatband potential (5, 18-20). In all of our studies of the collection efficiency, however, the disk potential was fixed at 1.0V vs. SCE , which is so positive that no oxygen reduction can occur.

The dependency of the oxygen collection efficiency, N_{O_2} [defined as $-i_R(E_R = -0.2\text{V})/i_D(E_D = 1.0\text{V})$ under illumination] upon total acetate concentration is shown in Fig. 3. No effect of electrode rotation rate was found with the concentrations of acetate shown in this figure. At very low concentrations of acetate (less than 1 mM) some effect of electrode angular velocity, ω , was observed however. As shown in Fig. 4, with 0.25 mM acetate the decrease in N_{O_2} was greater at larger ω , showing that at these concentra-

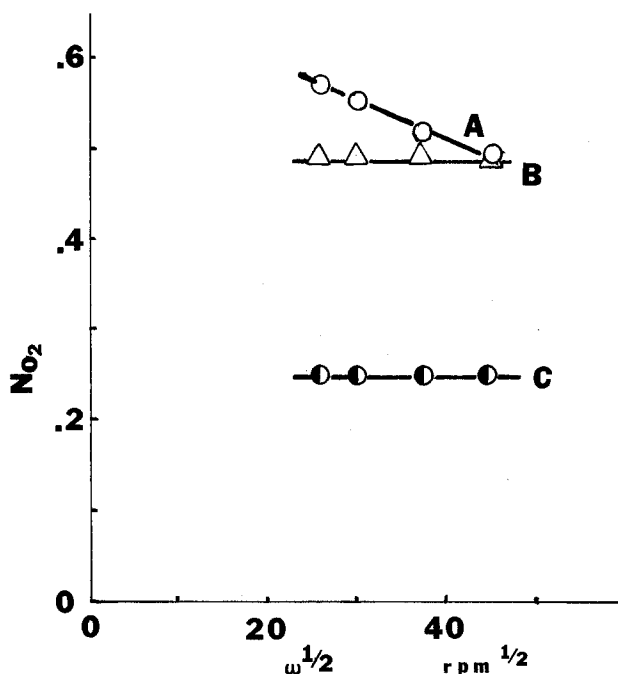


Fig. 4. Effect of rotation rate on the collection efficiency for oxygen in acetate solutions. (Curve A) 0.25 mM acetate; (curve B) 1 mM acetate; (curve C) 0.06M acetate. $E_D = 1.0\text{V vs. SCE}$; $E_R = -0.2\text{V vs. SCE}$.

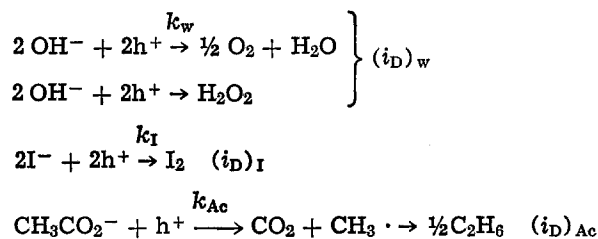
tions the rate of mass transfer of acetate to the disk governs its rate of oxidation.

Iodide solutions.—In the presence of I^- , oxidation of this species competes with water oxidation at the irradiated TiO_2 disk (2, 3). Because concentrations of I^- as low as $10^{-7}M$ suppress the oxygen reduction reaction on platinum, the addition of only small amounts of I^- decrease N_{O_2} to negligible values. To determine the competition between the water and I^- oxidation processes in this case, the ring current due to iodine reduction was determined (Fig. 5) and from this the iodine collection efficiency, N_{I_2} [defined as $-i_R'(E_R = -0.2V)/i_D(E_D = 1.0V)$ in the presence of I^-], was calculated. The variation of N_{I_2} , for solutions in the absence and presence of acetate, as a function of the concentration of sodium iodide is shown in Fig. 6. No effect of ω on N_{I_2} was observed for these concentrations of iodide ion.

Discussion

The reactions which give rise to the different disk and ring currents can be summarized as follows

Disk:



Under conditions where mass transfer rates to the disk surface are unimportant, we assume that the rate of consumption of a given species at the electrode surface is a first-order process (just as most electrochemical reactions) with relative rate constants of k_w , k_I , and k_{Ac} for water, iodide, and acetate, respectively. Under these conditions the total disk current, i_D , can be represented as

$$i_D = (i_D)_w + (i_D)_I + (i_D)_{Ac} \quad [6]$$

$$i_D = k_w[OH^-] + k_I[I^-] + k_{Ac}[Ac^-] \quad [7]$$

For solutions of acetate (in the absence of iodide) the ring current for oxygen reduction is

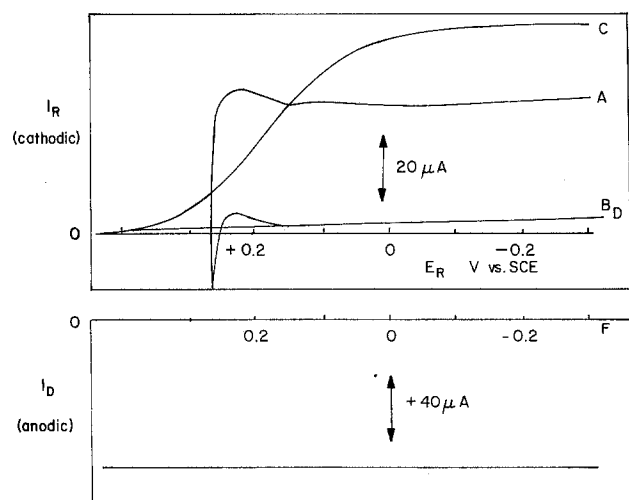


Fig. 5. Current-potential curves for Pt-ring electrode with illuminated $n-TiO_2$ disk electrode. (Curve A) 0.01M NaI under illumination; (curve B) 0.01M NaI in the dark; (curve C) no NaI under illumination; (curve D) no NaI in the dark; (curve E) 0.01M NaI disk current under illumination; (curve F) 0.01M NaI disk current in the dark. $E_D = 1.0V$ vs. SCE; rotation rate, 700 rpm; potential scan rate, 22 mV/sec.

$$-i_R = N_o(i_D)_w = N_o k_w [OH^-] \quad [8]$$

and the collection efficiency is

$$N_{O_2} = \frac{-i_R}{i_D} = \frac{N_o k_w [OH^-]}{k_w [OH^-] + k_{Ac} [Ac^-]} \quad [9]$$

This equation can be rearranged to the form

$$(N_o/N_{O_2}) - 1 = (k_{Ac}/k_w [OH^-]) [Ac^-] \quad [10]$$

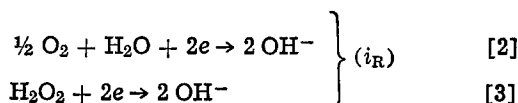
A plot of $N_o/N_{O_2} - 1$ vs. $[Ac^-]$ should be linear with zero intercept and slope $k_{Ac}/k_w [OH^-]$. Such a plot is shown in Fig. 7. From the slope of the line and the solution pH (4.7) a value of $k_{Ac}/k_w = 2.0 \times 10^{-8}$ is obtained.

A similar treatment for iodide solutions (in the absence of acetate) yields

$$N_{I_2}/N_o = k_I [I^-] / (k_w [OH^-] + k_I [I^-]) \quad [11]$$

so that the slope of a plot of $(N_o/N_{I_2}) - 1$ vs. the reciprocal of the iodide concentration should yield k_w/k_I . Such a plot at pH = 5.8 (shown in Fig. 8, curve

Ring:



A) yields $k_w/k_I = 8.8 \times 10^5$. The current efficiency for iodide oxidation at illuminated TiO_2 has previously been studied and for a 0.01M iodide solution has been estimated as 60% (3) and 70% (2). From the value of k_w/k_I found here, a current efficiency of 65% is predicted, which is in good agreement with the previous values.

For solutions containing both iodide and acetate, the following equation holds

$$\frac{N_{I_2}}{N_o} = \frac{k_I [I^-]}{k_w [OH^-] + k_I [I^-] + k_{Ac} [Ac^-]} \quad [12]$$

In this case a plot of $(N_o/N_{I_2}) - 1$ vs. $[I^-]^{-1}$ at a constant acetate concentration has a zero intercept and a slope of $(k_w/k_I) [OH^-] + (k_{Ac}/k_I) [Ac^-]$. Such a plot is shown in Fig. 8, curve B, for a 0.5M total acetate solution at pH = 4.7. The experimental slope combined with the value of k_w/k_I determined above yields $k_{Ac}/k_w = 4.5 \times 10^{-8}$ which is in reasonable agreement

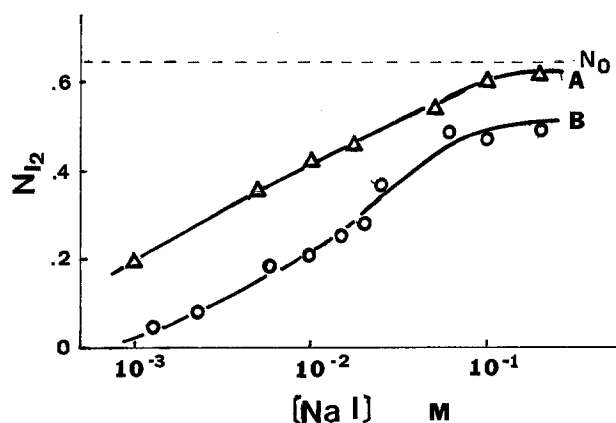


Fig. 6. Dependence of collection efficiency for iodine on the concentration of sodium iodide. (Curve A) no acetate; (curve B) 0.5M acetate; $E_D = 1.0V$ vs. SCE; $E_R = -0.2V$ vs. SCE; rotation rate, 700 rpm.

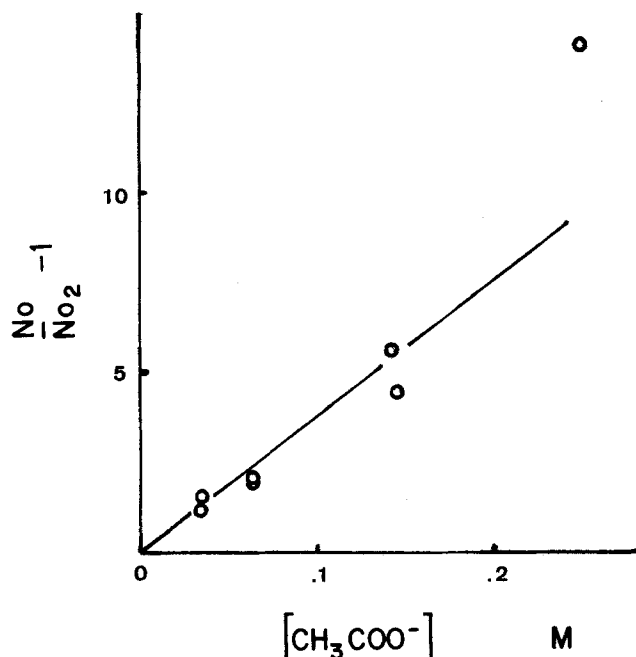


Fig. 7. Reciprocal plot on NO_2 and acetate concentration with the value found from Fig. 7. The relatively good agreement of the experimental results with the theo-

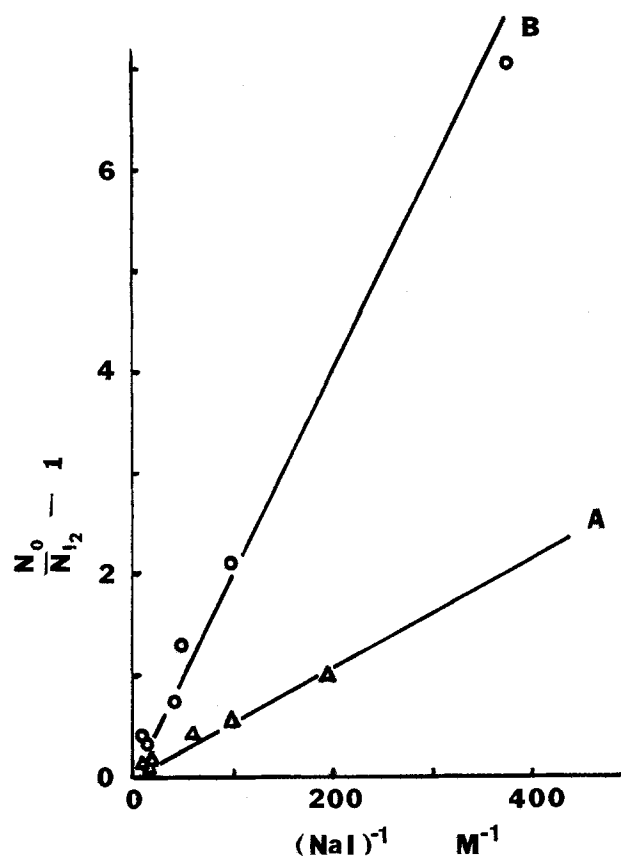


Fig. 8. Reciprocal plot of N_{12} and iodide concentration. (Curve A) no acetate; (curve B) 0.5M acetate.

retical equations suggests that there is no direct interaction of the oxidation processes, i.e., that k_w , k_{Ac} , and k_f are independent of the concentrations of acetate and iodide in the solution.

The results above demonstrate the utility of the RRDE technique in determining competitive reaction rates at an illuminated semiconductor, even when, as in the case of acetate above, the product generated is not electroactive at the ring electrode. The method is clearly easier for surveying possible reactions at semiconductors than long-term bulk electrolysis methods, and should also prove useful in the design of heterogeneous photocatalysts (6, 7).

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