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Oxidative Properties of Quinolinium Dichromate[1]

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Abstract—In acid medium, quinolinium dichromate oxidized aromatic acids to the corresponding hydroxybenzoic acids, and dicarboxylic acids to the corresponding semialdehydes. The rate of the reaction showed a first order dependence on the concentrations of substrate, oxidant and acid. For the oxidation of the aromatic acids, the rate-determining step involved the formation of a cyclic chromate ester, which underwent decomposition to give the product. In the case of dicarboxylic acids, the mechanistic pathway was via the formation of the intermediate acyclic chromate ester which underwent decomposition, in the slow step, to give the product.

INTRODUCTION

Earlier investigations had reported the decarboxylation of aromatic acids using different oxidizing agents, and the products obtained were mainly phenols [1–10]. The periodate oxidation of salicylic acid had yielded 1,4-benzoquinone-2-carboxylic acid [11]. However, kinetic aspects on the oxidation of aromatic acids have not received much attention.

The kinetics and mechanism of the oxidation of dicarboxylic acids have been studied using oxidants such as vanadium (V) [12], Co(III) [13], $S_2O_8^{2-}$ [14], and Ce(IV) in acid medium [15–17]. However, the mechanistic pathways described in these investigations did not give any clear evidence for the nature of either carbon-carbon or carbon-hydrogen bond fission.

With a view to highlight the kinetic features of these oxidations reactions and to examine the nature of the products obtained, we have investigated the oxidation of: (i) aromatic acids (salicylic acid and substituted salicylic acids), and (ii) dicarboxylic acids (glutaric and adipic acids) by quinolinium dichromate [QDC, $(C_9H_7NH^+) \cdot 2Cr_2O_7^{2-}$], in acid medium, under a nitrogen atmosphere. This study forms part of our sustained efforts to exploit QDC for the oxidation of organic substrates [18].

EXPERIMENTAL

Materials, methods and stoichiometry

Salicylic acid (S.D. fine Chemicals Co.), 3-hydroxybenzoic acid, 4-hydroxybenzoic acid, 2,4-dihydroxybenzoic acid, glutaric acid (SRL), and adipic acid (HPC) were recrystallized before use. Quinolinium dichromate (QDC) was prepared by the reported method [19], and its purity checked by spectral analysis. The infrared spectrum (KBr) exhibited bands at 930, 875, 765, and 730 cm^{-1}, characteristic of the dichromate ion. Sulfuric acid (E. Merck) was used after a check of its physical constants. Acetic acid (S.D., AR grade) was distilled under reduced pressure and the fraction distilling at 116°C was used. Dimethylformamide (DMF) was obtained from Spectrochem and was distilled under reduced pressure. Salicylic acid-d^6 was prepared by the reported method [20]. Deuterium oxide was obtained from the Aldrich Chemical Company. The IR spectra were recorded using the FT-IR (DA-8, Bomem) spectrophotometer.

All the kinetic measurements were performed under nitrogen, using pseudo-first-order conditions, with [substrates] ≫ [QDC]. The method of evaluating rate constants (reproducibility ±3%) has been described earlier [18]. The stoichiometries of the reactions were determined [18] to be:

$$3C_7H_6O_3 + 2Cr(VI) + 3H_2O \longrightarrow 3C_7H_6O_4 + 2Cr(III) + 6H^+, \quad (1)$$

(Salicylic acid)

$$C_5H_8O_4 + 2Cr(VI) + H_2O \longrightarrow C_4H_6O_3 + CO_2 + 2Cr(IV) + 4H^+. \quad (2)$$

(Glutaric acid)

[1] This article was submitted by the authors in English.

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Table 1. Rate data for the oxidation of aromatic and dicarboxylic acids at 323 K

[Substrate] × 10^2, M	[QDC] × 10^3, M	[H_2SO_4], M	k_1^* × 10^4, s^{-1}				k_1^{**} × 10^5, s^{-1}	
			salicylic acid (**1**)	3-hydroxy-benzoic acid (**2**)	4-hydroxy-benzoic acid (**3**)	2,4-dihydroxy-benzoic acid (**4**)	glutaric acid	adipic acid
1.0	1.0	3.0	0.37	0.18	0.29	1.15	0.038	0.019
5.0	1.0	3.0	1.86	0.91	1.51	5.53	0.190	0.090
10.0	1.0	3.0	3.57	1.85	3.03	11.2	0.381	0.187
20.0	1.0	3.0	7.54	3.65	6.12	22.5	0.764	0.378
5.0	0.75	3.0	1.88	0.92	1.52	5.52	0.191	0.092
5.0	0.50	3.0	1.86	0.93	1.51	5.51	0.194	0.093
5.0	0.25	3.0	1.87	0.95	1.56	5.57	0.192	0.090
5.0	1.0	3.0	1.84	0.93	1.55	5.54	0.191	0.096
5.0	1.0	3.5	2.15	1.06	1.74	6.39	–	–
5.0	1.0	4.0	2.50	1.20	2.04	7.34	0.248	0.122
5.0	1.0	4.5	2.77	1.36	2.28	8.22	–	–
5.0	1.0	5.0	3.12	1.50	2.51	9.15	0.296	0.158

* Solvent: H_2O/AcOH = 50 : 50 (vol).

** Solvent: H_2O.

Product analysis

Water (30 ml) was taken and cooled in ice. Concentrated H_2SO_4 (4.2 ml) was added slowly with constant cooling. When the acid solution had cooled to room temperature, quinolinium dichromate (0.5 M) was added and the mixture warmed to 323 K for complete dissolution of the QDC. To this mixture, 0.5 M of substrate (1.73 g salicylic acid, 1.73 g 3-hydroxybenzoic acid, 1.73 g 4-hydroxybenzoic acid, 1.93 g 2,4-dihydroxybenzoic acid, 1.65 g glutaric acid and 1.83 g adipic acid), taken in 25 ml of 50% water-acetic acid and 25 ml of 50% water-DMF solutions, respectively (for aromatic acids and dicarboxylic acids), was added. The reaction mixture was stirred at 323 K for 24 h under nitrogen for completion of the reaction. The organic layer was extracted with ether (3 × 25 ml), and the organic extracts were washed with water and dried over anhydrous Na_2SO_4. The oxidized products (2,6-dihydroxybenzoic acid from salicylic acid; 2,3-dihydroxybenzoic acid from 3-hydroxybenzoic acid; 2,4-dihydroxybenzoic acid from 4-hydroxybenzoic acid; 2,4,6-trihydroxybenzoic acid from 2,4-dihydroxybenzoic acid; succinic semialdehyde from glutaric acid; and glutaric semialdehyde from adipic acid), were obtained after complete removal of ether (melting points were in agreement with literature values; yields ≈80–85%). Each product was characterized by IR (KBr) analysis:

(i) 2,6-dihydroxybenzoic acid: ν = 3448 (b, s, –OH), 3030 (s, ArH str.), 2630 (O–H str.), 1695 (s, C=O), 1613, 1493, 1389 (O–H bend.), 1215 (C–O, str.), 910 (O–H str), 820 cm^{-1}.

(ii) 2,3-dihydroxybenzoic acid: ν = 3571 (b, s, –OH), 3030 (s, ArH str.), 2630 (O–H str.), 1670 (s, C=O), 1613, 1471, 1370 (O–H bend.), 1200 (C–O, str.), 900 (O–H str.), 752 cm^{-1}.

(iii) 2,4-dihydroxybenzoic acid: ν = 3450 (b, s, –OH), 3040 (s, ArH str.), 2610 (O–H str.), 1680 (s, C=O), 1610, 1350 (O–H bend.), 1220 (C–O, str.), 890 (O–H str.), 780 cm^{-1}.

(iv) 2,4,6-trihydroxybenzoic acid: ν = 3580 (b, s, –OH), 3060 (s, ArH str.), 2670 (O–H str.), 1650 (s, C=O), 1620, 1370 (O–H bend.), 1210 (C–O, str.), 900 (O–H str.), 790 cm^{-1}.

(v) Succinic semialdehyde: ν = 3265, 2981 (br s, –OH), 1712 (s, C=O), 1669, 1202, 920 cm^{-1}.

(vi) Glutaric semialdehyde: ν = 3279, 2988 (br s, –OH), 1705 (s, C=O), 1660, 1240, 928 cm^{-1}.

RESULTS AND DISCUSSION

Kinetic Results

The pseudo-first-order rate constant (k_1) did not change appreciably with changing QDC concentrations

(10-fold range), at constant substrate concentration (large excess), indicating a first-order dependence on QDC (Table 1). The reactions were first-order in substrate and acid (Table 1). The linear increase in the rate of oxidation with $[H^+]$ indicated the involvement of a protonated Cr(VI) species. These data suggested the following rate law:

$$w = k[\text{substrate}][\text{QDC}][H^+].$$

The oxidation reactions were studied in solutions containing varying proportions of solvent mixtures (water–acetic acid and water–DMF). The dielectric constants (D) of the solvent mixtures were calculated from the dielectric constants of the pure solvents (at 323 K: water = 69.94, acetic acid = 6.29, DMF = 37.6) [21]. It was observed that a decrease in D resulted in an increase in the rate of the reaction (Tables 2–3). Plots of $\log k_1$ versus $1/D$ were linear with positive slopes, suggesting the possibility of an ion-dipole type of interaction [22].

The rates of oxidation of these acids were increased in D_2O medium (Table 4), in agreement with earlier reported observations [23]. If the solvent isotope effect had been less than unity, then this would have indicated a pre-equilibrium proton transfer process. Since D_3O^+ is about three times stronger than H_3O^+ [23, 24], the solvent isotope effect being greater than unity suggested a proton-catalyzed reaction. This supported the protonation of the QDC, an observation reflected in the acid dependence on the rates (Table 1).

The oxidation of the substrates, under nitrogen, did not induce the polymerization of acrylonitrile [25], ruling out a one-electron oxidation. Control experiments, done in the absence of the substrate, did not show any appreciable change in [QDC].

The effect of temperature has been shown in Table 5. The negative values of ΔS provided support for a polar bimolecular reaction.

Mechanism

At concentrations of acid larger than 0.05 M (range of $[H_2SO_4]$ used was 3.0–5.0 M), the dichromate ion was shown to be the predominant species [26]. Earlier reports have established the involvement of a protonated chromium (VI) species in chromic acid oxidation reactions [27].

The data in Tables 2–3 (decrease in the dielectric constant of the medium resulting in an increase in the pseudo-first-order rate constant), suggests the absence of decarboxylation. This experimental observation is significant in view of the fact that a reduction in the pseudo-first-order rate constant with decreasing D has been used as evidence to support the process of decarboxylation [5]. Thus, a change in D of the solvent medium affected the rate by decreasing the concentration of available protons required for decarboxylation.

Table 2. Solvent effect for oxidation of aromatic acids by QDC at 323 K

H_2O/AcOH (%, v/v)	D	$k_1 \times 10^4$, s^{-1}			
		1	**2**	**3**	**4**
50 : 50	38.1	1.86	0.91	1.51	5.53
45 : 55	34.9	2.69	0.94	1.83	7.09
40 : 60	31.8	4.17	1.38	2.30	9.12
35 : 65	28.6	6.92	1.57	3.46	12.9
30 : 70	25.4	12.0	2.01	5.10	19.9

Note: [Substrate] = 0.05 M, [QDC] = 0.001 M, $[H_2SO_4]$ = 3.0 M.

Table 3. Solvent effect for the oxidation of glutaric and adipic acids at 323 K

H_2O/DMF (%, v/v)	D	$k_1 \times 10^5$, s^{-1}	
		glutaric acid	adipic acid
100 : 0	69.94	0.190	0.090
95 : 5	68.32	0.321	0.143
90 : 10	66.71	0.526	0.220
85 : 15	65.09	0.839	0.361
80 : 20	63.47	1.462	0.560

Note: [Substrate] = 0.05 M, [QDC] = 0.001 M, $[H_2SO_4]$ = 3.0 M.

Table 4. Solvent isotope effects at 323 K

Substrate	$k_1 \times 10^4$, s^{-1}		k^{D_2O}/k^{H_2O}
	k^{H_2O}	k^{D_2O}	
1	1.86	3.07	1.65
2	0.91	1.38	1.52
3	1.51	2.45	1.62
4	5.53	8.68	1.57

Note: [Substrate] = 0.05 M, [QDC] = 0.001 M, $[H_2SO_4]$ = 3.0 M.

The effect of substituents can be used to support a bimolecular reaction pathway. Successive substitution of the hydroxyl group into the *ortho* and *para* positions resulted in an increase in the rate of the reaction, in the series **2 < 3 < 1 < 4** (Table 1). The addition of the hydroxyl group in the *ortho* and *para* positions resulted in a decrease in the enthalpy of activation from 57 to 42 kJ mol^{-1} (Table 5). The lower rate of oxidation of salicylic acid (as compared to that of 2,4-dihydroxybenzoic acid), could be attributed to the presence of the hydroxyl group in the *ortho* position which would influence the distribution of charge as a result of the steric configuration. This steric arrangement would not be possible either with 3-hydroxy- or with 4-hydroxybenzoic acids. Since inductive and resonance effects

Table 5. Dependence of rate constants on temperature and activation parameters

$T \pm 0.1$, K	$k_1 \times 10^4$, s^{-1}				$k_1 \times 10^5$, s^{-1}	
	1	**2**	**3**	**4**	glutaric acid	adipic acid
313	0.87	0.46	0.72	3.50	0.095	0.044
318	1.23	0.65	1.03	4.51	0.137	0.065
323	1.86	0.91	1.51	5.53	0.190	0.090
328	2.40	1.36	1.99	7.38	0.275	0.129
333	3.31	1.98	2.84	9.75	0.382	0.181
$\Delta H^{\neq}$, (kJ mol^{-1})	55 ± 2.2	61 ± 2.4	57 ± 2	42 ± 2.3	55.1 ± 2.5	55.8 ± 2.4
$\Delta S^{\neq}$, (J mol^{-1} K^{-1})	–147 ± 6	–135 ± 5	–145 ± 6	–180 ± 5	–177 ± 6.4	–181 ± 4.5

Note: [Substrate] = 0.05 M, [QDC] = 0.001 M, $[H_2SO_4]$ = 3.0 M.

are expected to be similar for the *ortho* and *para* isomers, it could be postulated that steric considerations exerted a critical influence on the rate of the reaction, resulting in a lower rate for the oxidation of salicylic acid (Table 1).

The dissociation constant of glutaric acid is 4.58×10^{-5} ($pK_1 = 4.34$), and that of adipic acid is 3.71×10^{-5} ($pK_1 = 4.43$) in the experimental range of temperatures studied [21]. These values are quite low, and it can be concluded that these acids remained undissociated in the presence of the high concentrations of mineral acid used in the present investigation.

In the oxidation of dicarboxylic acids by one-electron oxidants such as V(V) and Mn(III) pyrophosphate, the reaction proceeded via a radical intermediate [12], although the postulation of a radical intermediate and the reported second-order dependence on V(V) and Mn(III) concentrations seemed to be in direct conflict. Indeed, the involvement of a radical intermediate in the Ce(IV) oxidation of dicarboxylic acids did not show a second-order dependence on the concentration of Ce(IV) ions [28, 29]. In the present investigation, a first-order dependence on [QDC] has been established (Table 1), without any evidence for radical formation.

An alternate route to hydroxylation could be considered as proceeding via the reaction of an enol intermediate. If this were so, then the enolization of the dicarboxylic acids should be much faster than their rates of oxidation by QDC (for the enol to be considered as a possible reactive intermediate). For this purpose, the rates of enolization of these acids were measured, using the bromination method. At $[H^+]$ = 3.0 M and 323 K, the values of k_{en} were found to be 9.3×10^{-5} s^{-1} (for glutaric acid) and 4.4×10^{-4} s^{-1} (for adipic acid). These values were about 50 times faster than the first-order oxidation rates for glutaric acid and adipic acid, respectively, at 323 K (Table 1). This experimental observation made it amply clear that the rate of enolization of these dicarboxylic acids was extremely fast compared to their rates of oxidation by QDC. This was further substantiated by the first-order dependence of the rate on [QDC], which established that the step involving the formation of the enol intermediate was not rate-determining.

Table 6. Kinrtic isotope effect at 323 K

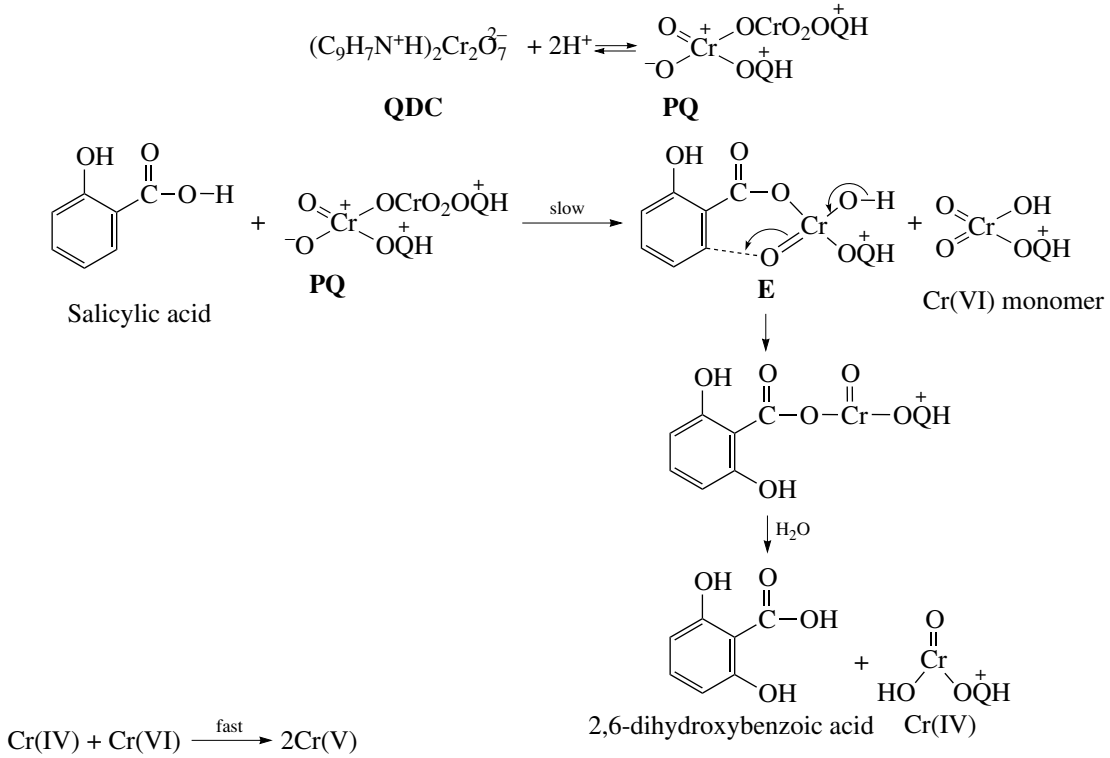
Substrate	$k_1 \times 10^4$, s^{-1}	k^H/k^D
Salicylic acid	1.86	–
Salicylic acid-d_6	0.78	2.4

Note: [Substrate] = 0.05 M, [QDC] = 0.001 M, $[H_2SO_4]$ = 3.0 M.

In an attempt to establish a correlation between structure and reactivity of these dicarboxylic acids, it was observed that the rate of oxidation of adipic acid was slower than that for glutaric acid (Table 1). The presence of an additional CH_2 group in adipic acid would hinder the formation of the chromate ester, thus reducing the concentration of the ester. This would result in the slowing down of the rate of oxidation of adipic acid, as compared to that for glutaric acid.

The sequence of reactions for the oxidation of aromatic acids is shown (Scheme 1). The attack of the protonated QDC (*PQ*) on the substrate (*S*) is crucial, and would be favored by the formation of the cyclic chromate ester (*E*). In order to test the feature of a cleavage of the carbon-hydrogen bond in the rate-determining step of the reaction, an evaluation of the kinetic isotope effect for the hydrogen atom in salicylic acid-d^6 was carried out. The data in Table 6 showed that salicylic acid reacted faster than salicylic acid-d^6 by a factor of 2.4, which indicated that the rate-determining step of the reaction involved a cleavage of the carbon-hydrogen bond. One could envisage a mechanism involving the formation of a cyclic intermediate in which the carbon (of the substrate) was bonded to the oxygen (of the oxidant). This involved six electrons; being a Hückel-type system ($2n + 2$), this was an allowed process [30]. The oxidation rate for the organic acids was not increased as rapidly by a decrease in the water concentration in water–acetic add mixtures (Table 2), suggesting that a molecule of water was not involved in a kinetically important stage of the oxidation reaction.

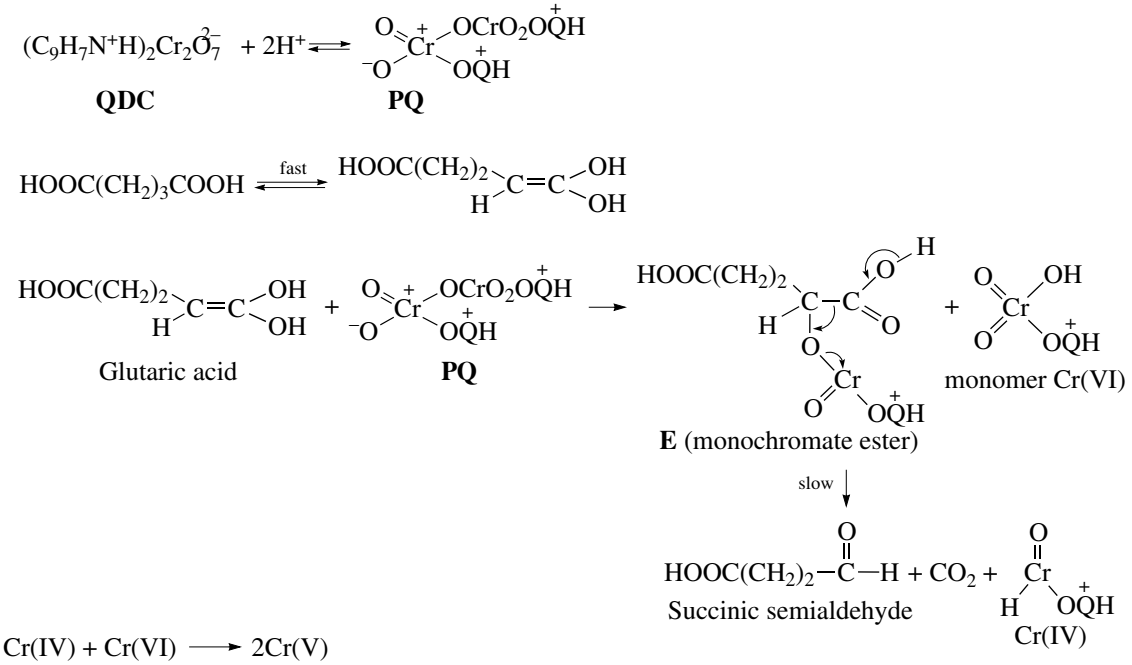
The sequence of reactions for the oxidation of dicarboxylic acids by QDC is shown (Scheme 2). In acid medium, QDC was converted to the protonated dimetallic chromium(VI) species (*PQ*). The substrate was rapidly converted to the enol form (*S*), which then reacted with *PQ*, resulting in the formation of an acy-



$$Cr(IV) + Cr(VI) \xrightarrow{fast} 2Cr(V)$$

$$Cr(V) + substrate \xrightarrow{fast} product + Cr(III)$$

Scheme 1.



$$Cr(IV) + Cr(VI) \longrightarrow 2Cr(V)$$

$$Cr(V) + substrate \longrightarrow product + Cr(III)$$

Scheme 2.

clic monochromate ester (*E*), which underwent decomposition, in the rate-determining step, to give the product. The absence of a primary deuterium kinetic isotope effect ruled out the rate-limiting C–H bond cleavage (using α-deuteroglutaric acid, $k^H/k^D = 1.05$; using α-deuteroadipic acid, $k^H/k^D = 0.98$). The kinetic data and the nature of the products obtained thus established that the rate-determining step was the breaking of the carbon–carbon bond (Scheme 2).

The conversion of Cr(IV) to Cr(III) proceeds via a disproportionation reaction. For the reaction Cr(IV) + Cr(VI) $\longrightarrow$ 2Cr(V), an extremely favorable standard potential for the Cr(VI)–Cr(V) couple ($E^0 = 0.62$ V) facilitated this reaction [31]. The Cr(V)–Cr(III) couple ($E^0 = 1.75$ V), enabled the rapid conversion of Cr(V) to Cr(III), after the reaction of Cr(V) with the substrate [31, 32].

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