Electrochemical oxidation of aliphatic hydrocarbons promoted by inorganic radicals. II. NO_3 radicals

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The anodic electrolysis of linear alkanes in tert-butanol/H_2O solutions containing HNO_3 and saturated with oxygen at $P_{O_2} = 1$ atm results in the partial oxidation of the hydrocarbons to the corresponding isomeric ketones. The experimental data are in support of a mechanism in which the first steps are: (1) one-electron transfer from the nitrate ion to the anode to give a nitrate radical; (2) hydrogen abstraction by the nitrate radical on the aliphatic substrate to give an alkyl radical; (3) molecular oxygen addition by the alkyl radical and formation of peroxy radicals. These species decay by bimolecular reactions and a carbonyl function is formed. The isomer distribution is in excellent accord with a statistical H abstraction from the secondary C–H bonds.

1. Introduction

Partial anodic oxidation of aliphatic hydrocarbons has been extensively investigated in non-aqueous and in highly acidic media [1–6]: the initial products of the electrode reaction are carbonium ions generated through the fission of a carbon–hydrogen bond. These carbonium ions are very reactive and their life time strongly depends on the nucleophilic properties of the solvent; furthermore, in the case of n-alkanes some rearrangements of the intermediates often occur. Other than with the solvent, carbonium ions may react with added nucleophiles such as water, acetic acid, nitriles and alcohols. In particular in the non-nucleophilic FSO_3H solvent with CH_3COOH added [6], α–β unsaturated ketones with two more carbon atoms than the starting materials were produced by CH_3CO^+ insertion on the rearranged form of the carbonium ions. However, in partially aqueous systems saturated ketones were produced from alkanes by simultaneous electrolytic reduction of molecular oxygen and a Fe(III) salt [7]. In this process the primary products at the electrode are

Fe(II) ions and H_2O_2; from their reaction OH radicals are generated, and by H atom abstraction the hydrocarbons are activated towards the oxygen insertion.

To overcome the kinetic limits due to the molecular oxygen reduction, we considered it appropriate to examine the direct electrodic generation of other simple radical species able to abstract H atoms from the alkane. Some inorganic radicals generated in the anodic electrolysis of the corresponding negative ions were considered first. Among those examined the NO_3 radical appeared to be particularly promising.

2. Experimental procedures

The chemicals used were reagent grade products.

The electrochemical cell was equipped in the anodic compartment with a Pt net (5% Ir, 45 mesh, surface $25\,cm^2$) and a commercial saturated calomel electrode (SCE) (Ingold) as reference against which all potential values in this paper are quoted, In the cathodic compartment a helical platinum wire was the counter

electrode. The anodic compartment, separated from the cathodic by a salt bridge, was filled with $10\,cm^3$ of the examined hydrocarbon, $15\,cm^3$ of tert-butyl alcohol and $1.5\,cm^3$ of 65% HNO_3. In the case of C_8–C_{10} hydrocarbons $8\,cm^3$ of alkane and $17\,cm^3$ of alcohol were utilized to avoid phase separation. This solution was stirred using a magnetic stirrer and was maintained under O_2 saturation at atmospheric pressure by a slow bubbling of high purity oxygen. At the end of the electrolysis (usually 250 C of charge transferred, current density of about $3\,mA\,cm^{-2}$) the solution contained in the anodic compartment of the cell was neutralized by $NaHCO_3$ and analysed by gas phase chromatography. The chromatographic columns and analytical conditions were as follows:

Pentane: 25 m OV 1; temperature programme, $50°$ for 5 min, then at $2°\,min^{-1}$ to $80°$ for 5 min; internal standard 1-pentanol.

Hexane, heptane and octane: 25 m FFAP, temperature programme $50°$ for 5 min, then at $2°\,min^{-1}$ to $80°$ for 12 min; internal standard 1-hexanol.

Nonane: 25 m FFAP, temperature programme, $50°$ for 5 min, then at $2°\,min^{-1}$ to $90°$ for 15 min; internal standard 1-heptanol.

Decane: 25 m FFAP, temperature programme, $60°$ for 5 min, then at $2°\,min^{-1}$ to $90°$ for 15 min; internal standard 1-hexanol.

The column used had an internal diameter of 0.3 mm; the carrier gas was hydrogen at 0.25 atm.

Electrochemical yields were calculated on the basis of a consumption of 1F per mole of products.

3. Results and discussion

Fig. 1 shows the voltammetric curves obtained in tert-butyl alcohol containing 0.82 M HNO_3 as supporting electrolyte, with and without hydrocarbon addition (see curves a and b, respectively). The curve c was obtained under similar conditions to curve a, substituting $HClO_4$ for HNO_3.

It emerges clearly that at potentials $\gtrsim 1.8\,V$, NO_3^- ions are involved in the anodic process. This is fully in accordance with the data reported
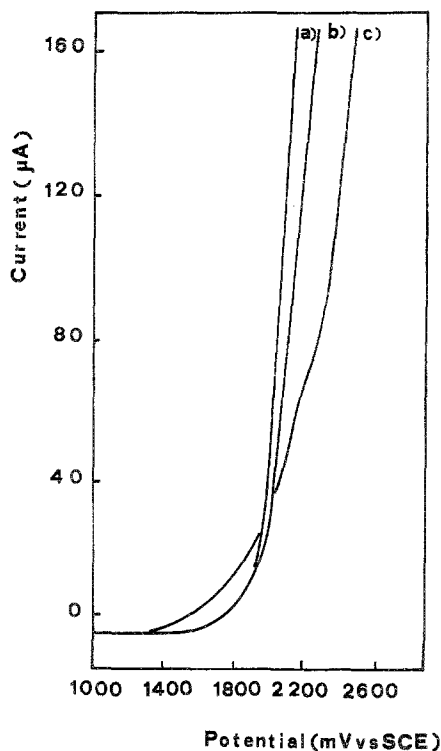

Fig. 1. Voltammetric curves obtained by a Pt sphere microanode (area $0.026\,cm^2$) and a potential scan rate of $3.3\,mVs^{-1}$. Curve a; $30\,cm^3$ tert-butyl alcohol + $1.8\,cm^3$ 65% HNO_3. Curve b; $18\,cm^3$ tert-butyl alcohol + $1.8\,cm^3$ 65% HNO_3 + $12\,cm^3$ n-heptane. Curve c; $30\,cm^3$ tert-butyl alcohol + $1.73\,cm^3$ 70% $HClO_4$. t = $30°$.

by other authors on the electrochemical properties of NO_3^-, which presents an oxidation potential $E_{1/2}$ of about 2.1 V vs SCE [8–13]. Moreover, there is experimental evidence that nitrate radicals generated at the anode from NO_3^- ions are involved in the electrochemical oxidation of methylated aromatic hydrocarbons [14–15]. In particular, the direct oxidation of aliphatic compounds such as linear hydrocarbons or tert-butyl alcohol can be excluded when the anode potential is kept in the range 1.8–2.5 V since the $E_{1/2}$ for the oxidation of these compounds are $\gtrsim 3\,V$.

On these bases a series of n-alkanes were electrolytically oxidized in the presence of 0.82 M HNO_3 at anodic potentials in the range 1.8–2.5 V.

The gas phase chromatographic analyses of the reaction products show the formation of isomeric ketones with current yields ranging
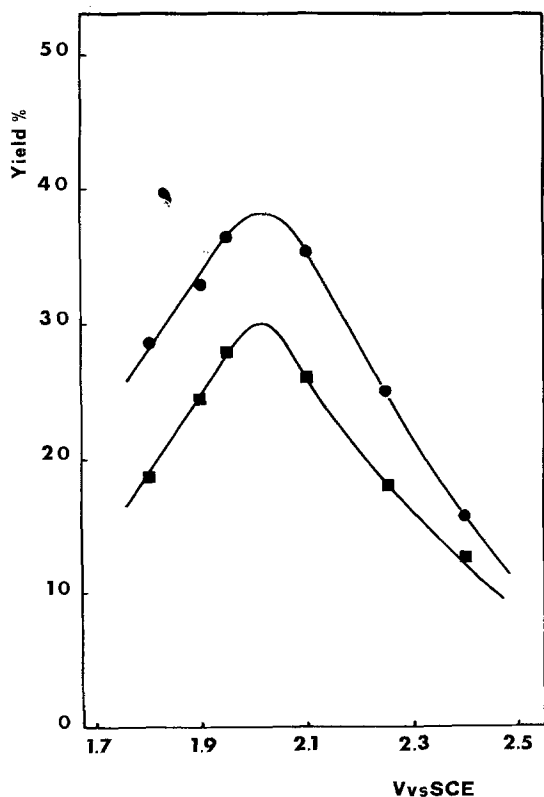
Fig. 2. Pentane: current yields of 2- and 3-pentanone as a function of the anode potential at 20°. ●, 2-pentanone; ■, 3-pentanone.
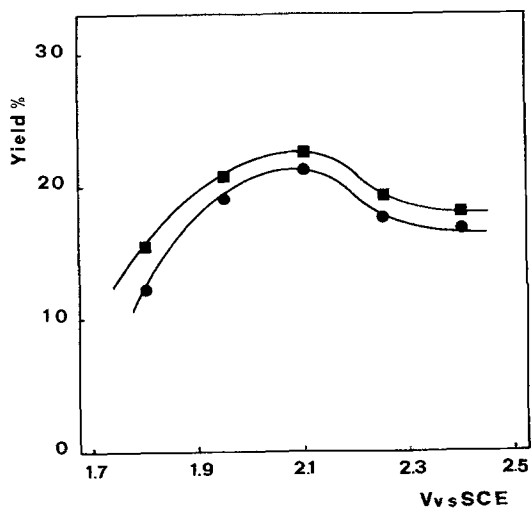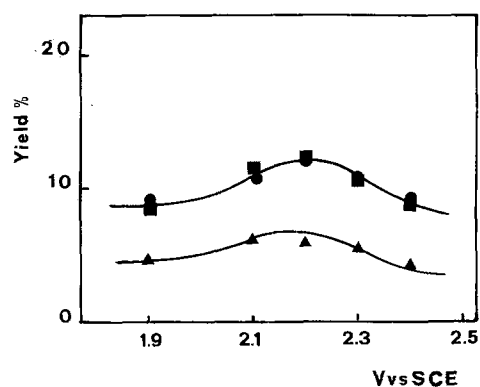

Fig. 4. Heptane: current yields of 2-, 3- and 4-heptanone as a function of the anode potential at 30°. ●, 2-heptanone; ■, 3-heptanone; ▲, 4-heptanone.

from about 30 to 100%. The yields of the different isomeric ketones obtained from each hydrocarbon examined are reported in Figs 2–7 as a function of the anode potential. A common characteristic of these plots is the presence of a maximum of the current yield in the potential range 2.0–2.3 V. By comparison with the plots of Fig. 1 it emerges that the potential range of this maximum corresponds to the rising portion of the i–E curve of NO_3^- discharge (curve b).

An indirect confirmation of the radical nature of the products generated from NO_3^- ions in the course of the electrolysis was obtained in experiments with benzene and toluene as oxidizable substrates. The reaction products were biphenyl and benzaldehyde, while no traces of nitro-aromatic compounds were found. The latter

Fig. 3. Hexane: current yields of 2- and 3-hexanone as a function of the anode potential at 30°. ●, 2-hexanone; ■, 3-hexanone.
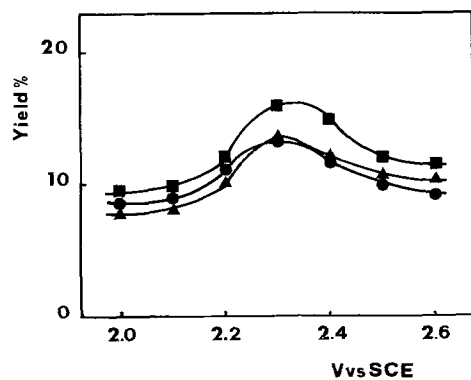

Fig. 5. Octane: current yields of 2-, 3- and 4-octanone as a function of the anode potential at 30°. ●, 2-octanone; ■, 3-octanone; ▲, 4-octanone.
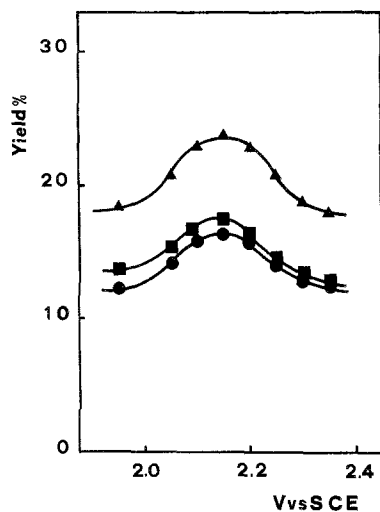
Fig. 6. Nonane: current yields of 2-, 3-, 4- and 5-nonanone as a function of the anode potential at 30° C. ●, 2-nonanone; ■, 3-nonanone; ▲, 4- plus 5-nonanone.

compounds were those expected on the hypothesis of NO_3^- oxidation to NO_2^+ ion [9]. Moreover, when $HClO_4$ was substitued for HNO_3 in the electrolysis solution the alkane oxidation did not occur.

The decrease of the ketone yields at potentials higher than 2.3 V would be a consequence of the increasing contribution of H_2O oxidation to the total current (see Fig. 1).

In Table 1 the distribution of the isomeric ketones obtained at different electrolysis potentials is reported; this distribution is roughly independent of the applied potential in the range 1.8–2.4 V. At potentials lower than 1.8 V the electrolysis current falls to a negligible value; by contrast, the current density attains very high values for $E \geqslant 2.4$ V. From Table 1 it emerges that there is generally good agreement between the experimental and theoretical data calculated on the basis of a statistical H atom abstraction from the secondary C–H bonds of the alkane.

In Fig. 8 the total yields of the pentanones and nonanones are reported as a function of the hydrocarbon concentration, working at an anode potential of 2.1 V and in the presence of 0.82 M HNO_3. The plots indicate that the yields increase monotonically with the hydrocarbon concentration. This behaviour indicates that the hydrocarbons are not directly oxidized at the anode but that they compete for a primary elec-
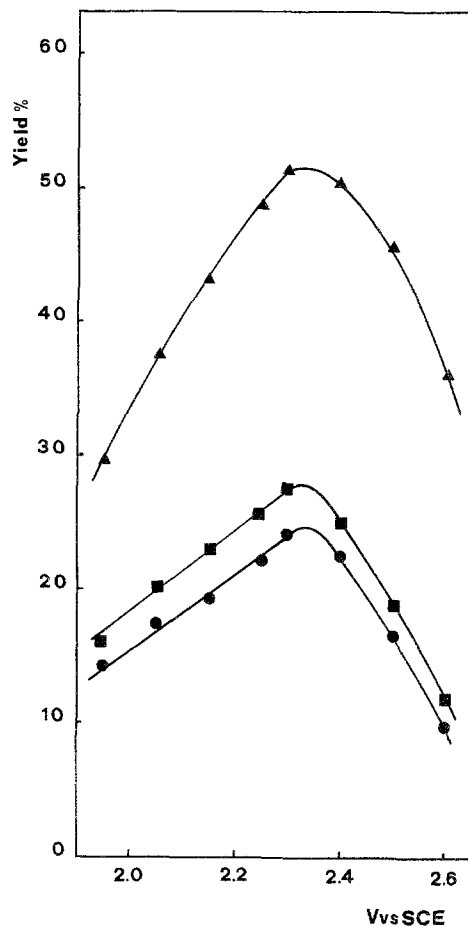

Fig. 7. Decane: current yields of 2-, 3-, 4- and 5-decanone as a function of the anode potential at 30°. ●, 2-decanone; ■, 3-decanone; ▲, 4- plus 5-decanone.

trodic product which in our case is the NO_3 radical.

In Fig. 9 the dependence of the pentanone yield on the HNO_3 concentration is reported. In the range of concentration examined there is a continuous increase of the ketone yield with the acid concentration. This is in accord, as discussed before, with the simultaneous anodic oxidation of H_2O and NO_3^-. In fact, with increase in the concentration of the latter species the current fraction engaged in the H_2O oxidation decreases with a consequent increase of the yields of NO_3 radical production.

In Fig. 10 the maximum yield of ketones is reported for each hydrocarbon as a function of the number of carbon atoms. In these experiments the weight ratio hydrocarbon/tert-butyl

Table 1. The dependence of molar ratios of isomeric ketones on the electrolysis potentials. In the right hand column theoretical yields, based on a statistical H abstraction from all the secondary C–H bonds, are reported

Ketone	Electrolysis potential (V)						Theoretical ratios
	1.9	2.0	2.1	2.2	2.3	2.4	
2-pentanone	0.58	0.56	0.58	0.58	0.59	0.59	0.67
3-pentanone	0.42	0.44	0.42	0.42	0.41	0.41	0.33
2-hexanone	0.49	0.48	0.48	0.48	0.47	0.48	0.50
3-hexanone	0.51	0.52	0.52	0.52	0.53	0.52	0.50
2-heptanone	0.40	0.39	0.40	0.39	0.40	0.42	0.40
3-heptanone	0.39	0.39	0.38	0.39	0.40	0.42	0.40
4-heptanone	0.21	0.22	0.22	0.22	0.20	0.16	0.20
2-octanone	–	0.33	0.33	0.34	0.31	0.30	0.33
3-octanone	–	0.36	0.36	0.36	0.37	0.38	0.33
4-octanone	–	0.31	0.31	0.30	0.32	0.32	0.33
2-nonanone	0.28	0.28	0.28	0.28	0.28	0.28	0.286
3-nonanone	0.31	0.31	0.31	0.30	0.30	0.30	0.286
4-nonanone⎱ 5-nonanone⎰	0.41	0.41	0.41	0.42	0.42	0.42	0.428
2-decanone	0.23	0.23	0.23	0.23	0.23	0.23	0.25
3-decanone	0.28	0.27	0.27	0.26	0.27	0.26	0.25
4-decanone⎱ 5-decanone⎰	0.49	0.50	0.50	0.51	0.50	0.51	0.50

alcohol decreases from about 0.55 (C_5–C_7 alkanes) to about 0.45 (C_8–C_{10}). On the contrary the ratio (weight of –CH_2– groups)/(weight of –CH_2– plus CH_3– groups) increases from about 0.55 (C_5–C_7 alkanes) to about 0.65 (C_8–C_{10}). As a consequence pentane and decane, for instance, should show a very similar reactivity towards the NO_3 radicals under our experimental conditions. The anomalous behaviour we obtained may indicate that other physicochemical parameters should be considered, such as adsorption at the platinum electrode [16].

In general the results indicate that the oxidation of the alkanes via NO_3 radicals as intermediates leads to the same type of oxidized
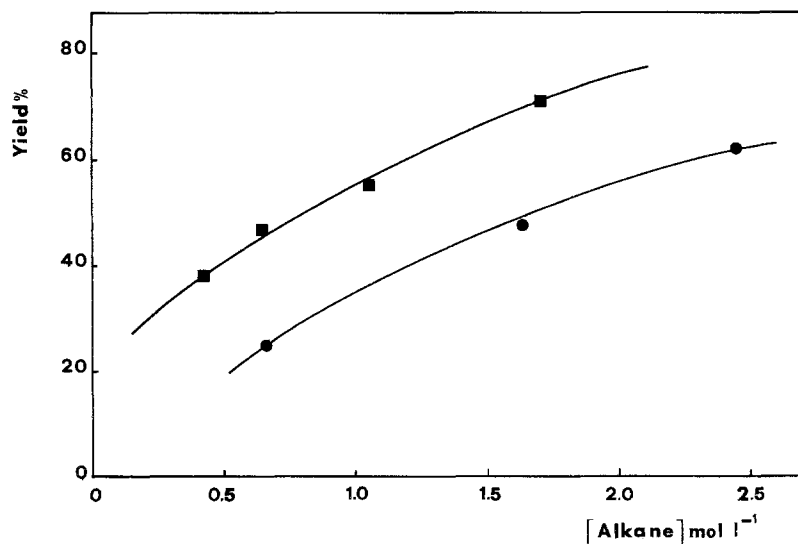

Fig. 8. Current yields of isomeric pentanones and nonanones as a function of the molar concentration of parent alkane at 2.1 V, 0.82 M HNO_3, t = 30°. ●, pentanones; ■, nonanones.
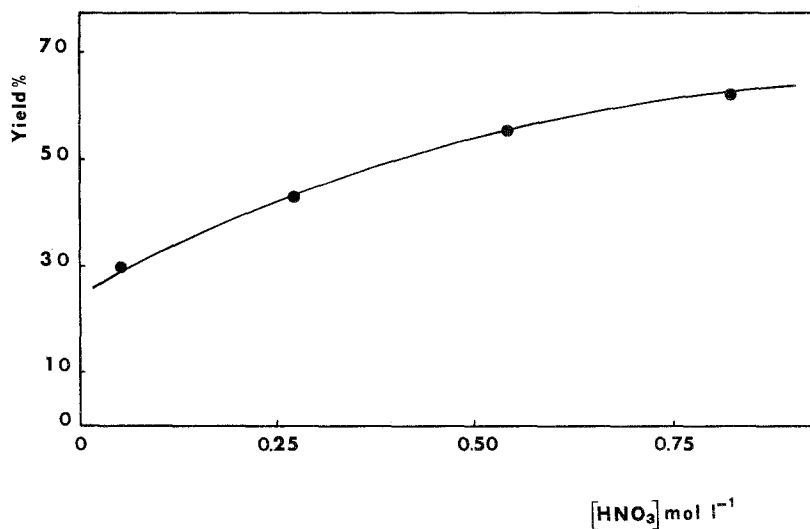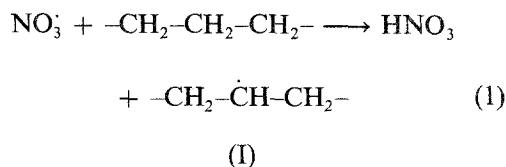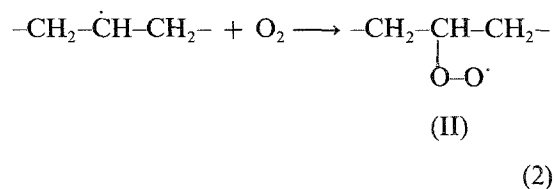
Fig. 9. Current yields of isomeric pentanones as a function of the molar concentration of HNO_3 at 2.1 V, t = 20°.

products obtained with OH radicals [7]. Consequently it is reasonable to hypothesize that the same mechanism is involved: that is, the primary formation of alkyl radicals (I) from the alkanes by H atoms abstraction

$$NO_3^{\cdot} + -CH_2-CH_2-CH_2- \longrightarrow HNO_3$$
$$+ -CH_2-\overset{\cdot}{C}H-CH_2- \qquad (1)$$
$$(I)$$

followed by molecular oxygen addition,

$$-CH_2-\overset{\cdot}{C}H-CH_2- + O_2 \longrightarrow -CH_2-\underset{\underset{O-O^{\cdot}}{|}}{C}H-CH_2-$$
$$(II)$$
$$(2)$$

The peroxy radical (II) produces a carbonyl group as a product of bimolecular self reaction, as previously reported [7]:

$$2-CH_2-\underset{\underset{O-O^{\cdot}}{|}}{C}H-CH_2- \longrightarrow 2-CH_2-\underset{\underset{O}{||}}{C}-CH_2- + P$$
$$(3)$$
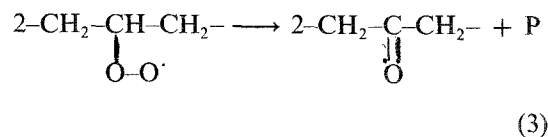
in which P indicates the products O_2, HO_2, H_2O_2.
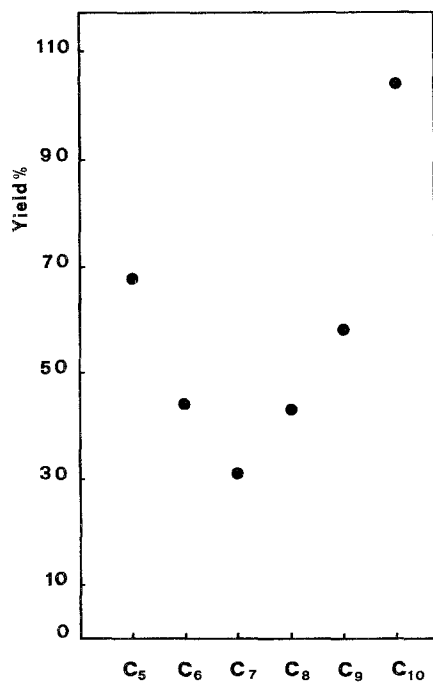
Acknowledgement

Fig. 10. Maximum current yield of oxidation products of the alkanes as a function of the number of carbon atoms. The values are deduced from the data of Figs 2–7.

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