

# Plasma Polymerization of Some Simple Saturated Hydrocarbons

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## Synopsis

Methane, ethane, propane, and *n*-butane were polymerized in a plasma created by a radio-frequency glow discharge. It was found that the kinetics of polymer deposition were similar for all monomers but methane. It is suggested that the deviation from "normal" behavior of methane may be due to the difference in mechanism of formation of reaction intermediates. The "characteristic map" for the plasma polymerization of ethane was determined. It was shown that, in addition to transparent films, powders may be formed at low pressures and low monomer flow rates and unstable discharges at high pressures and low flow rates. With increasing power input, the unstable regions are decreased while the powdery regions are increased. The rates of polymer deposition were found to depend on pressure, flow rate, and power. An empirical equation is proposed that relates the rates of deposition for ethane, propane, and *n*-butane to these parameters.

## INTRODUCTION

In conventional polymerization reactions, the presence of some kind of functional groups such as double bonds is generally required of the chemical structure of monomers. However, in the case of formation of polymers in the plasma created by a low-pressure electric discharge, virtually any organic or organometallic vapor with or without functional groups can be polymerized.<sup>1,2</sup> In plasma polymerizations, the process is initiated by the collisions between energetic free electrons in the plasma with the monomer molecules to form active species. These active species may be ions or excited molecules but more predominantly are free radicals.<sup>3-6</sup> They then react either with themselves or with virgin monomers to form polymers both in the gas phase and on adjacent surfaces in the reactor. In previous publications from this laboratory, preliminary data on the plasma polymerization of saturated hydrocarbons were reported.<sup>6,7</sup> In this work, further investigations in this regard will be carried out in an effort to shed some light on the kinetics and mechanism of these unique reactions.

## EXPERIMENTAL

Chemically pure-grade methane, ethane, propane, and *n*-butane were purchased from the Matheson Gas Products Company and were used as received. A tubular plasma polymerization reactor was employed throughout this study.<sup>8</sup> The schematic diagram for the reactor is shown in Figure 1. Essentially, it

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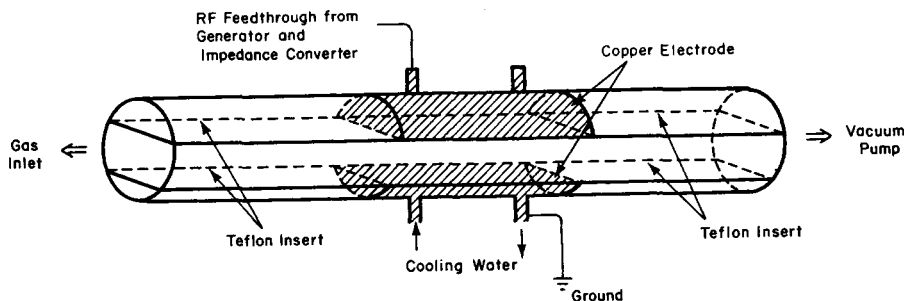


Fig. 1. Schematic diagram of the tubular flow plasma reactor.

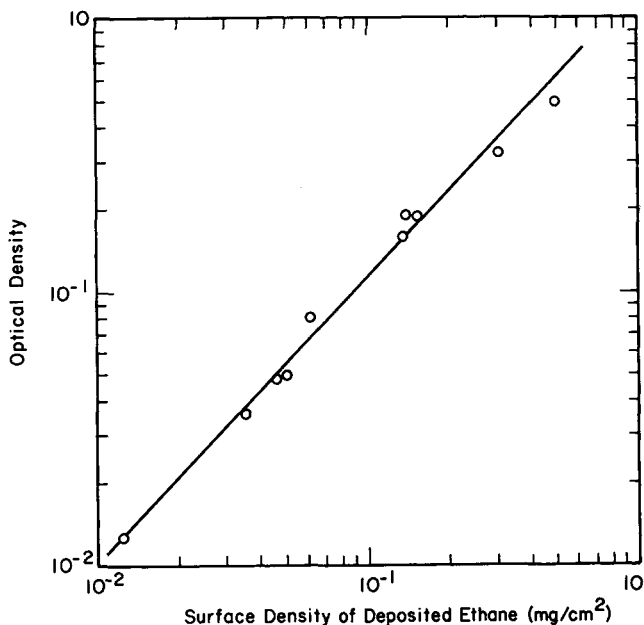


Fig. 2. Optical density of plasma-polymerized ethane determined at  $3.4 \mu\text{m}$  (C—H stretching frequency) plotted vs surface density determined by weighing method.

consists of two parallel electrodes in a glass tube. The bottom electrode is cooled by circulating water. Monomer gas is supplied through a circular fritted distributor on one end of the reactor. Evacuation is effected by a mechanical pump from the other end. Power is supplied by an International Plasma Corporation Model PM401 radio-frequency generator at 13.56 MHz with a maximum output of 150 W.

Rates of polymer deposition were determined by two methods. In the first method, thin aluminum plates (0.1 mm thick) were placed on the lower electrode as the substrate. They were weighed on an analytic balance before and after each experiment to determine the amount of polymer deposited. In the second method, sodium chloride crystals were used as substrates. From the absorbance of the C—H stretching peak at  $3.4 \mu\text{m}$ , the amount of polymer can be found from a precalibrated curve. Figure 2 shows that the two methods yielded satisfactory agreement. Usually, the first method is preferred for large amounts of deposition, while the second method is more suitable for smaller quantities of polymers.

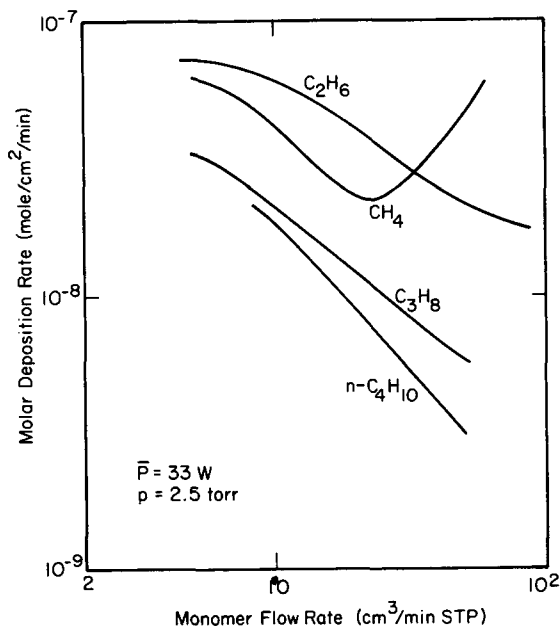


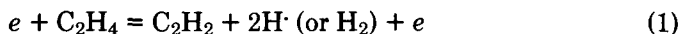
Fig. 3. Molar deposition rates for plasma polymerization of methane, ethane, propane, and *n*-butane at 33 W and 2.5 torr plotted as a function of monomer flow rate.

## RESULTS AND DISCUSSION

Figure 3 shows the molar rates of polymer deposition as a function of the rate of monomer supply at a fixed power level and pressure. The deposition rates are in the order  $C_2H_6 > C_3H_8 > C_4H_{10}$ . For ethane, propane, and *n*-butane, the deposition rates decrease with increasing flow rate. The general trend of decreasing deposition rates with increasing monomer feed rate is consistent with that observed in the plasma polymerization of other monomers.<sup>6-8</sup> The interpretation is that the residence times of the reactive species were decreased by the increased flow rate and that some of the reactive species were swept away before polymerization could take place. The anomalous case is that of methane, which first decreased in deposition rate to a minimum and then increased with flow rate. The observed behavior differs from that of other monomers and with the plasma polymerization of the same monomer in the bell jar reactor.<sup>6</sup>

Figure 4 shows the deposition rate data for the same four monomers as a function of power input. Because of the increased power input, one would expect larger numbers of active species to be present in the plasma and therefore enhanced rates of deposition. These data are in agreement with this expectation, except again for the case of methane, which shows a decrease in deposition rate at high levels of power input. As in Figure 3, the molar deposition rates decrease with increasing molecular weights of the monomers.

In our previous studies in the plasma polymerization of ethylene, it was proposed that acetylene is formed as a reaction intermediate<sup>6</sup>:



This mechanism is consistent with the conventional polymerization of ethylene in the gas phase.<sup>9</sup> Under comparable conditions, the rate of the plasma polymerization of ethylene is less than that of acetylene by about an order of mag-

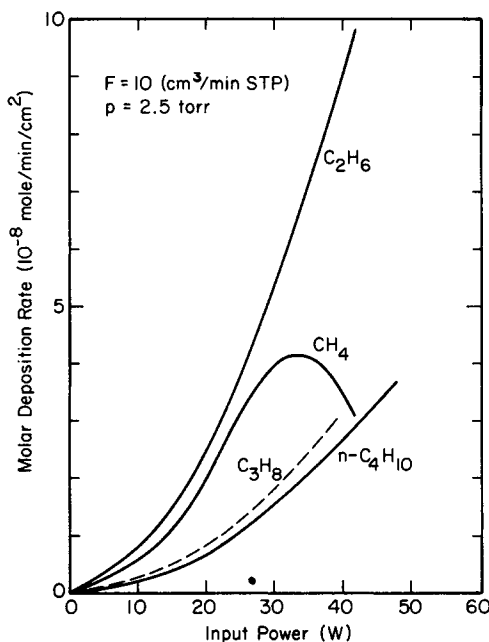


Fig. 4. Molar deposition rate for plasma polymerization of methane, ethane, propane, and *n*-butane at flow rate of 10 cc/min (S.T.P.) and pressure of 2.5 torrs plotted as a function of input power level.

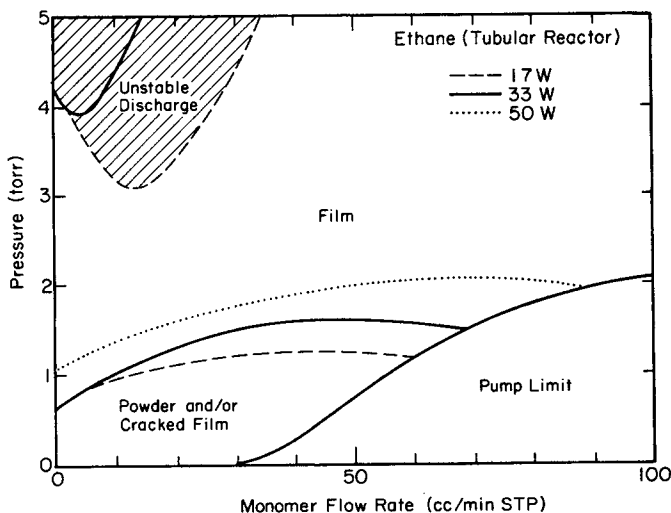
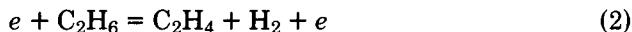


Fig. 5. Characteristic map for plasma polymerization of ethane in the tubular reactor.

nitide. The plasma polymerization of ethane is in turn slower than that of ethylene. Presumably, an extra step is required for the initial decomposition of ethane by electron impact to form ethylene first<sup>6</sup>:



which eventually form acetylene to undergo polymerization as in eq. (1). A similar mechanism may also be responsible for propane and *n*-butane. However,

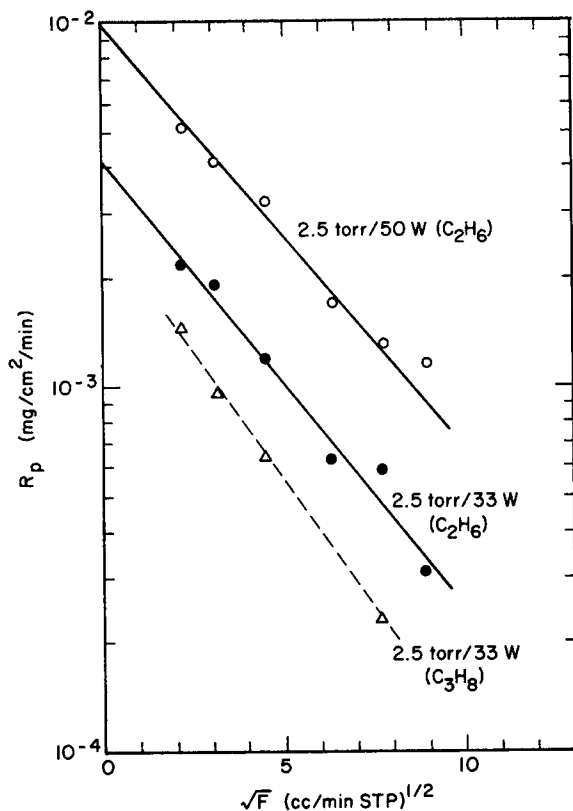


Fig. 6. Rates of deposition for plasma polymerization of ethane and propane plotted vs the square root of monomer flow rate.

in the case of methane, the absence of the C—C bond in the monomer rules out the type of mechanism exemplified by eq. (2). Indeed, photochemical data in the literature<sup>10,11</sup> have shown that the initial decomposition to diradicals is necessary for the formation of ethylene from methane. This difference in mechanism may be responsible for the observed difference in the kinetics of plasma polymerization of methane from the other saturated hydrocarbons.

Since we have already investigated the plasma polymerization of acetylene and ethylene in some detail, it would be of interest to further scrutinize the behavior of ethane polymerization for comparison. First, we show in Figure 5 the "characteristic map" for the plasma polymerization of ethane. It was found for ethylene that the form of the plasma polymer may be oil, film, or powder.<sup>12</sup> Two competing processes may be operative: one is the rate of propagation in the gas phase, and the other is the rate of diffusion of active species to the electrode surface from the plasma. If the polymerization rate is high, then the homogeneous reactions dominate in the gas phase to form powdery products. On the other hand, if the diffusion rate is greater, then heterogeneous reactions on the surfaces yield films and/or oils. For ethylene, all three forms of plasma polymer can be obtained, depending on the parameters used for the reaction. Acetylene polymerizes so rapidly that only powder can be obtained.<sup>6</sup> In the case of ethane, which polymerizes slowly in the plasma, films are formed under most conditions. Only at very low pressures and low flow rates can partial formation of powder

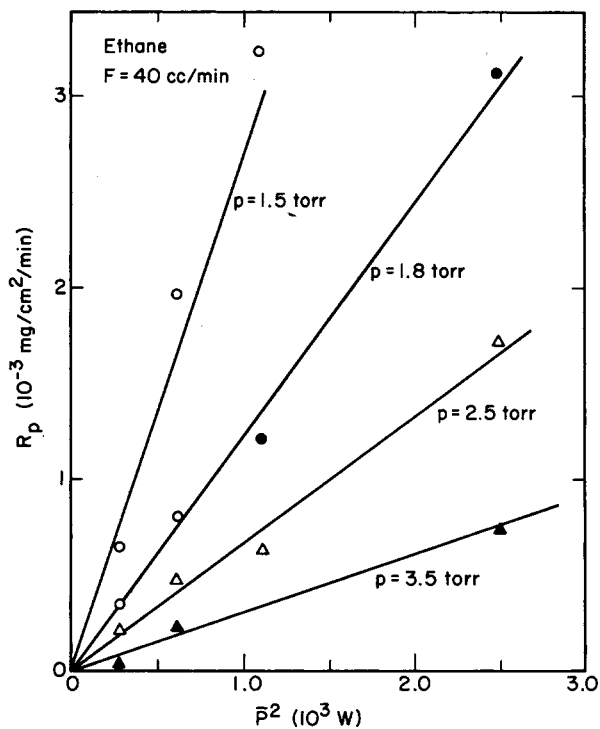


Fig. 7. Rate of deposition for plasma polymerization of ethane plotted vs the square of power input at a series of pressures.

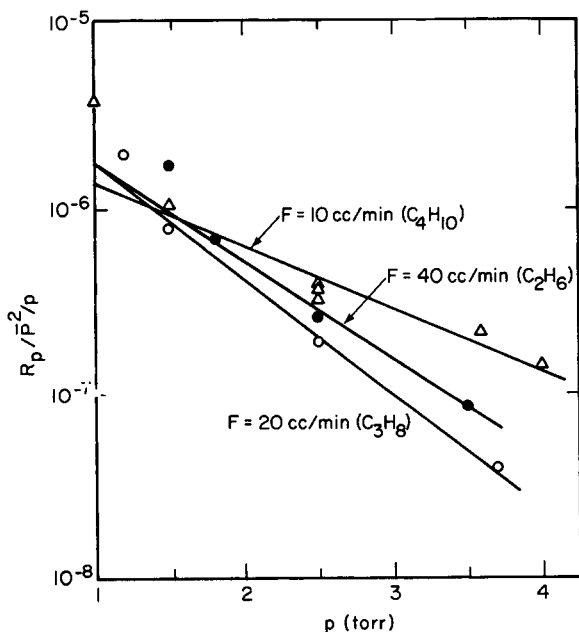


Fig. 8. Plot of  $R_p/\bar{P}^2/p$  vs pressure for plasma polymerization of ethane, propane, and *n*-butane.

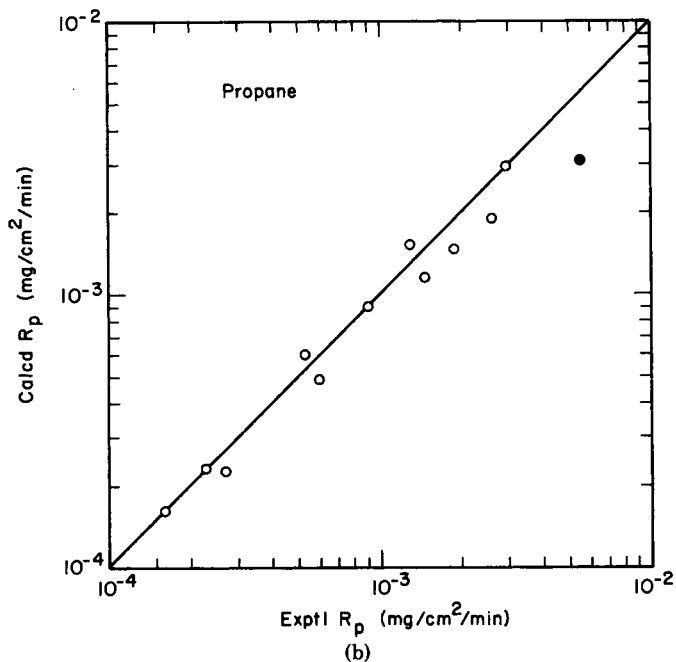
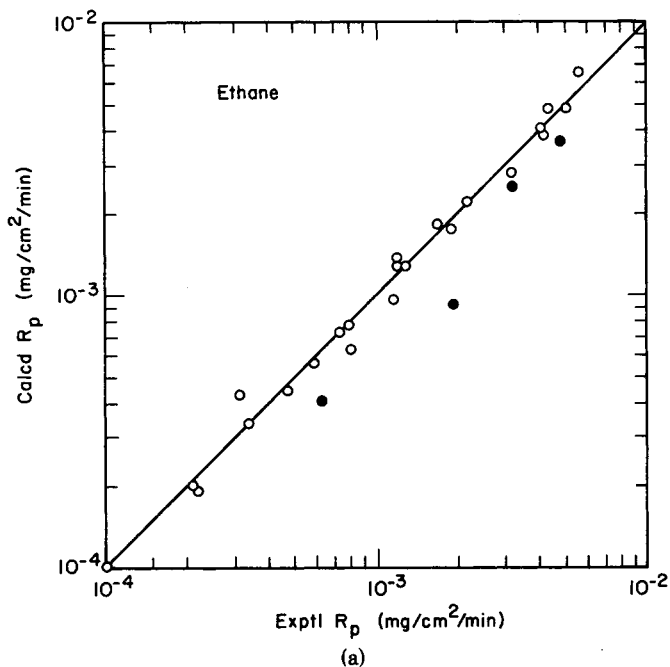


Fig. 9. Comparison of experimental and calculated rates of deposition for plasma polymerization of (a) ethane, (b) propane, and (c) *n*-butane. Open circles are data taken from the film regions, closed circles are from powder regions.

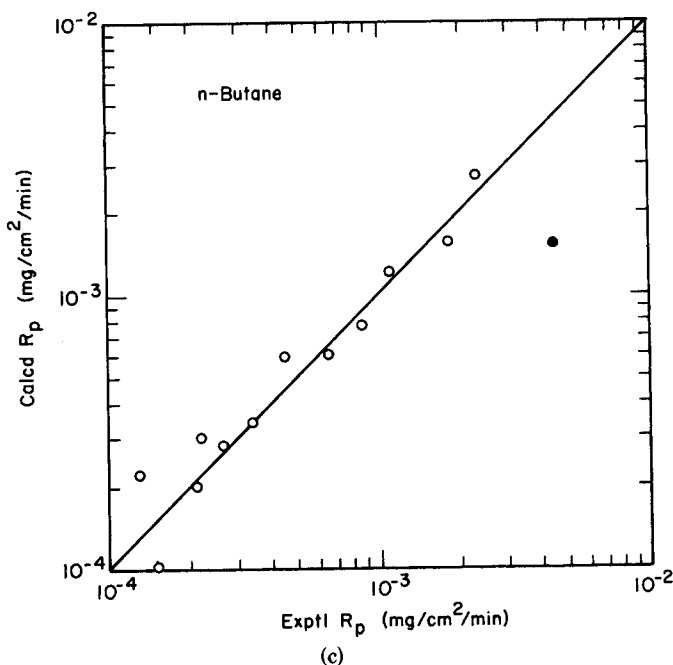


Fig. 9. (Continued from previous page.)

TABLE I  
Kinetic Constants for Plasma Polymerization of Simple Saturated Hydrocarbons

Constant	Ethane	Monomer Propane	<i>n</i> -Butane
$k_1, \text{mg/cm} \cdot \text{min} \cdot \text{torr} \cdot \text{watt}^2$	$2.97 \times 10^{-5}$	$3.05 \times 10^{-5}$	$1.62 \times 10^{-5}$
$k_2, \text{torr}^{-1}$	1.23	1.45	0.77
$k_3, \text{min}^{1/2}/\text{cc}^{1/2}$	0.25	0.29	0.54

be observed. The regions of powder formation are enlarged with increasing power input because of the enhanced population of active species. On the other hand, the regions of unstable discharge shrinks with increasing power, being negligible at 150 W. Presumably, at high rates of polymerization the powdery products in the gas phase act as electron sinks, thus rendering it difficult to sustain the discharge.

It has been shown in Figure 3 that the deposition rates ( $R_p$ ) for saturated monomers in log-log plots are nonlinear functions of monomer flow rates ( $F$ ). It is also shown that the  $R_p$  values are nonlinear functions of power input ( $\bar{P}$ ) in linear plots (Fig. 4). However, we have found that a linear relation is possible between  $\log R_p$  and the square root of flow rate ( $F^{1/2}$ ) for a number of plasma conditions (Fig. 6). In addition, we have also found linear relations between  $R_p$  and  $\bar{P}^2$ , as shown in Figure 7 for ethane.

To find the pressure dependence of  $R_p$ , we reason that the reaction rate must be proportional to the product of the monomer concentration and the radical concentration. The former can be represented just by  $p$ . For the latter, we



would expect the probability of collision of an electron with a gas molecule to be proportional to  $\exp(-K/\lambda)$ , where  $K$  is a constant and  $\lambda$  is the mean free path of the electron,<sup>13</sup> which should in turn be inversely proportional to pressure. If this rationalization is correct, then there should be a linear relationship between  $\log(R_p/\bar{P}^2 p)$  and  $p$ . Here, we have incorporated the  $\bar{P}^2$  dependence in order to use the data obtained at different power levels. Figure 8 shows, in fact, that the data seem to bear out this expectation. Thus, on the basis of these observations, we can write the following empirical equation for the plasma polymerization of saturated hydrocarbons:

$$R_p = k_1 \bar{P}^2 p \exp[-(k_2 p + k_3 F^{1/2})] \quad (3)$$

where the  $k$  values are empirical constants.

Comparisons of  $R_p$  values calculated by eq. (3) (using the empirical constants summarized in Table I) and those experimentally observed for ethane, propane, and *n*-butane are given in Figures 9(a)–9(c). The agreement is satisfactory for data obtained in film-forming regions of the characteristic map (open circles). Deviations are observed, however, for those determined in the powder-forming regions (closed circles). Thus, eq. (3) seems to be a useful empirical relation for the plasma polymerization of films from simple saturated hydrocarbons, even though there is a lack of theoretical justification. However, a model for this reaction has now been developed which is based on a more rigorous kinetic analysis and is amenable to computer calculations.<sup>14</sup> Nevertheless, eq. (3) has the virtue of simplicity, and calculations can be readily achieved without the recourse of a computer.

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