

tained a 70% yield of benzene and 53% of hydrogen. Since 15% of methane was formed it is evident that some sort of secondary chain reaction accompanies the main decomposition into benzene and hydrogen in spite of the low pressure. In these circumstances we feel that we cannot neglect the possibility that 1,3-cyclohexadiene may have been formed by a chain reaction in which a hydrogen atom is one of the chain carriers.

Summary

1. We have discussed the thermal decomposition of organic compounds from the standpoint of the principle of least motion and have pointed

out that organic decompositions may consist of a comparatively few elementary (*i. e.*, single step) reactions.

2. On heating cyclohexene oxide the main change is a rearrangement to cyclohexanone. This is accompanied by a decomposition of the cyclohexene oxide into water and a hydrocarbon, probably 1,4-cyclohexadiene.

3. 1,3-Cyclohexadiene decomposes into benzene and hydrogen.

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Reproducible Contact Angles on Reproducible Metal Surfaces. II. Interfacial Contact Angles between Water and Organic Liquids on Surfaces of Silver and Gold

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The angle formed at the line of contact of two liquids, such as water and an organic liquid, against a solid phase is generally referred to as an *interfacial contact angle*. Reliable data pertaining to interfacial contact angles could be of much importance, but such data as do exist are for the most part of questionable value, for seldom do data presented by different investigators show good agreement.

One difficulty which besets the investigator is that, for a given system, he may obtain different and *apparently* stable angles anywhere between two fairly wide limits. The limits of variation are the values of the angles which have usually been referred to as "advancing" and "receding" contact angles. This same variation exists also with contact angles of solid-liquid-air systems and has been discussed in an earlier paper.¹

In the majority of investigations the fact that the two liquids of a solid-liquid-liquid system possess at least limited miscibility has been largely disregarded. Furthermore, it appears that no one has given much consideration to the possibility that adsorption of the dissolved material might occur at either or both of the solid-liquid interfaces, nor to the fact that highly condensed and firmly held layers might be formed which could not easily be removed and which, by their presence, would cause considerable alteration of interfacial tension.

In the present investigation it has been quite

conclusively demonstrated that all of the factors mentioned above must be taken into consideration. In addition it has been shown that time must be allowed for any given system to attain equilibrium. Moreover, in case the experimental procedure is such as to bring about a slight displacement of the liquid-liquid interface at the line of contact with the solid, there then exists a tendency for a comparatively great readjustment of conditions at and near the line of intersection of the interfaces. Such readjustment would involve partial or total removal or deposition of condensed layers as well as both adsorption and desorption processes and might require considerable time before the reattainment of equilibrium.

The solid surfaces selected for study in the present investigation were silver and gold surfaces formed by vaporization and subsequent condensation on Pyrex tips.¹ The liquids were "conductivity" water and purified isoamyl alcohol, *n*-butyl acetate, benzene, α -bromonaphthalene and heptane. The interfacial contact angles were formed with each of these different organic liquids against water on the solids. To save time in attaining equilibrium conditions each pair of liquids (*i. e.*, water and each of the organic liquids) used in this research were mutually saturated before use and it is to be understood that when reference is made to one of the liquids it refers to that liquid as being saturated with the other liquid of the pair.

(1) Bartell and Cardwell, *THIS JOURNAL*, **64**, 494 (1942).

The apparatus used for the formation of the interfacial contact angles was described in an earlier paper.¹ This apparatus made possible the formation of water drops on metal surfaces immersed in organic liquid as well as of organic liquid drops on metal surfaces immersed in water. In recording contact angles *the convention has been observed of expressing the value as that obtained when measured through the water phase.*

The results obtained in this investigation have shown that for a given solid-liquid-liquid drop system there exist two definite, stable, closely reproducible, contact angles.

Stable Solid-Organic Liquid-Water Contact Angles.—In order to obtain a stable and reproducible contact angle with a drop of water on a solid immersed in an organic liquid, one must form the drop on a solid which was in a fresh and clean condition when it was immersed in the organic liquid and which had been allowed to remain for a sufficient time in the organic liquid before the water drop was formed. If left undisturbed after its formation, the water drop will spontaneously adjust itself so as to reach the *stable* water advancing angle provided the drop as initially formed had an initial advancing angle greater in value than the value of the *stable* water advancing angle. In case the water drop as initially formed had an advancing angle smaller in value than that of the *stable* water advancing angle, no movement of the drop will occur spontaneously until the system has stood awhile longer and the volume of the drop has been expanded by addition of water to such an extent that the contact angle becomes greater than the *stable* water advancing angle. The drop will then adjust itself so as to form the *stable water advancing* angle. This *stable* angle does not change with time nor with further addition of water to the drop.

If, after one obtains a *stable water advancing* (solid-organic liquid-water drop) contact angle, one progressively withdraws liquid from the water drop, causing it to decrease in volume, the angle will progressively decrease until finally a definite and *stable water receding* angle is obtained. The value of this angle remains constant even though the volume of the drop is materially altered by withdrawal of liquid and even though the line of contact of solid-liquid-liquid drop is caused to move inward to a considerable extent. This angle we have designated as the *stable water receding contact angle.*

The values obtained for stable angles of water drops are presented in Table I. The *stable* water advancing angles for each of the organic liquid-water systems have practically identical values for a given metal. For silver this value is approximately 128° and for gold approximately 117°. Earlier investigators have found a similar constancy of interfacial angles for corresponding systems with other solids.² The *stable* water receding angles for the different organic liquid systems on a given metal were not identical and, moreover, in each case they were considerably different from the *stable* advancing angle.

TABLE I
STABLE SOLID-ORGANIC LIQUID-WATER DROP CONTACT ANGLES

Organic liquid	Water angle on silver		Water angle on gold	
	Advancing	Receding	Advancing	Receding
Isoamyl alcohol	127	72	117	61
<i>n</i> -Butyl acetate	129	68	116	57
Benzene	129	58	116.5	45
α -Bromo-naphthalene	127	65	118	55
Heptane	127	58	116.5	45

TABLE II
STABLE SOLID-WATER-ORGANIC LIQUID DROP CONTACT ANGLES

Organic liquid	Water angle on silver		Water angle on gold	
	Advancing	Receding	Advancing	Receding
Isoamyl alcohol	126	71	117	59
<i>n</i> -Butyl acetate	129	68	115.5	57
Benzene	129	57	116	45
α -Bromo-naphthalene	126	65	116	55
Heptane	127	57	115.5	45

In the formation of stable interfacial contact angles by organic liquid drops on solids immersed in water the instructions for the formation of *stable* angles with drops of water can be used. For the use with the organic liquid drops the terms *advancing* and *receding* must be interchanged, however, since an *advancing* (*i. e.*, expanding) organic liquid drop produces a *receding* water angle. It must be kept in mind also that a spontaneous movement of the organic liquid drop, while giving a smaller angle through the organic liquid phase, will give a larger angle through the water phase which is the phase through which the contact angle measurements must be made.

The results obtained with organic liquid drops are given in Table II. It will be noted that for the different organic liquids on a given metal the *stable* water advancing angles were all practically identical.

(2) Bartell and Bartell, THIS JOURNAL, 56, 2205 (1934).

tical. The angles obtained for silver were, as before, somewhat larger than those obtained for gold. The water receding contact angle values were considerably smaller than the water advancing angle values and were not identical for all the different organic liquids. As was the case also for the water drop measurements, with the non-polar liquids benzene and heptane the receding angle values were the same for a given solid while with the heteropolar organic liquids the receding angle values varied according to the solubility of the organic liquids in water, the greater the solubility the larger the stable receding angle.

A comparison of the data of Tables I and II obtained by the two methods, the one using the water drop and the other using the organic liquid drop, shows that all the corresponding values for the two methods of operation agree within the limit of two degrees. Each value reported in the tables or in the text is the average of at least twenty measurements. The maximum deviation for individual measurements was $\pm 1.5^\circ$, but the deviation of many of the measurements was not more than $\pm 0.5^\circ$. Maximum deviation occurred in the measurement of angles having maximum difference in advancing and receding angle values.

Initial Solid-Liquid-Liquid Contact Angles.—When a water drop was formed upon a new and clean metal surface immediately after immersion of the metal in one of the organic liquids, the water advancing contact angle thus initially obtained was not the same as the stable water advancing angle. On the other hand, when a drop of one of the organic liquids was formed upon a new and clean metal surface immediately after immersion of the metal in water the water receding contact angle thus initially obtained was in all cases, except that of isoamyl alcohol, the same as the corresponding stable angle. Values obtained from measurements made on drops formed within two minutes after immersion of the metal are shown in Table III and are designated *initial angles*.

TABLE III
INITIAL INTERFACIAL CONTACT ANGLES

Organic liquid	Solid-organic liquid- water drop		Solid-water-organic liquid drop	
	Water advancing angle on		Water receding angle on	
	Silver	Gold	Silver	Gold
Isoamyl alcohol	107	83	79	65
<i>n</i> -Butyl acetate	111	88	69	58
Benzene	180	95	57	45
α -Bromo- naphthalene	151	108	65	55
Heptane	180	107	58	45

These initial angles were closely reproducible when identical methods of procedure were used, but they were not in all cases stable angles since some of them changed upon standing or upon addition of liquid.

Theory of Condensed Liquid Layers on Solids.

—The experiments on stable interfacial angles and on initial interfacial angles demonstrate clearly that there are two, and only two, stable contact angles for any one of these solid-liquid-liquid systems. One stable angle, the water receding angle, can be obtained (except for the liquid systems containing isoamyl alcohol which has the highest solubility in water of any of the organic liquids used) immediately after the mutually saturated immiscible liquids are brought into contact with the solid surface. The other stable angle, the water advancing angle, can be obtained only after these liquids have been allowed to stand in contact with the surface for an optimum period of time which is different for different systems. This indicates that alteration of surface properties at the solid-liquid interfaces must occur before *stable* water advancing interfacial angles can be obtained.

In the case of the stable receding angles, which are obtained immediately, the interface is moving over an area previously occupied by water. In the case of the advancing angles, where the stable advancing angle cannot be obtained immediately, the interface is moving over an area previously occupied by organic liquid. It seems probable that the organic liquids produce on the metals highly condensed and firmly held layers which take time for their formation, whereas water produces no such layers on the metals. The organic liquids used, with the exception of alpha bromonaphthalene which forms small angles, do not form contact angles when placed upon silver or gold in air. The work of adhesion of silver or gold against one of these liquids is greater than the work of cohesion of the liquid. As a result of the attraction of the liquid molecules to the solid phase, the liquid immediately adjacent to the solid apparently tends to become denser and to form, in effect, a condensed layer. The force of attraction may extend through a distance representing a number of molecular diameters. Water, which forms a fairly large contact angle both on silver and gold in air, apparently does not tend to form condensed layers on these metals since the work of adhesion of water against the metals is less than the work of cohesion of water.

Condensed layers formed on solids by the non-angle-forming liquids appear to be tenaciously held and not quickly removed from the solid surface by water. The time that elapsed between the measurements of the initial water advancing angles of Table III and the stable water advancing angles of Table I, shown in Table IV, appears to

TABLE IV

TIME NECESSARY FOR TRANSFORMATION OF INITIAL ADVANCING ANGLES TO STABLE ADVANCING ANGLES FOR SYSTEM SOLID-ORGANIC LIQUID-WATER DROP

Liquid-liquid system	Silver, hours	Gold, hours
Isoamyl alcohol-water	2	1
<i>n</i> -Butyl acetate-water	4	1
Benzene-water	>72	11
α -Bromonaphthalene-water	12	2
Heptane-water	12	2

be approximately the length of time which was necessary for formation of the fully condensed organic liquid layers on the solid plus the time (*i. e.*, in those cases in which the initial contact angles are larger than the stable contact angles) for the water to partially remove this condensed organic liquid so as to give the stable water advancing contact angle. The shortest time was required for isoamyl alcohol (slightly less than one hour with gold) and the longest time was required for benzene (over 72 hours with silver). The water drop in the silver-benzene-water system had not broken through the benzene layer at the end of seventy-two hours as was evidenced by the fact that at the end of that time the contact angle was still approximately 180°. The value of 129° reported in Table I for the stable water advancing angle of the silver-benzene-water system was obtained on a silver surface which had been immersed in benzene no longer than half a minute before the water drop was formed.

The time required for producing stable interfacial water advancing angles formed by receding drops of organic liquids upon the metal surfaces immersed in water was much shorter than the time required for producing the corresponding angles by means of advancing water drops. In general it was found that the systems which required the shortest time to give the stable water advancing angle when the water drop was used required the longest time to give the stable water advancing angle when a corresponding organic liquid drop was used. Drops of heptane, α -bromonaphthalene and benzene on silver gave stable angle values if the organic liquid drops were re-

ceded within a few seconds, while with drops of *n*-butyl acetate and isoamyl alcohol it was necessary to let the drops stand for a period of about one minute. If the drops of benzene and heptane were allowed to stand on the solid for an hour or more before being withdrawn, the water advancing contact angles thus obtained approached 180°. As with the water drop system, if the benzene was allowed to remain in contact with the metal too long before the water was advanced over it, the water did not sufficiently remove the firmly held organic liquid layer, at least within any reasonable period of time, to give the stable advancing interfacial contact angles.

Adsorption Effects.—Some adsorption of water from the organic liquid phase at the solid-organic liquid interface probably occurs, but in the systems studied such adsorption is probably less than the adsorption of organic liquid from the water phase at the solid-water interface. Any effect due to adsorption appears to be of much smaller magnitude than the effects due to condensed layers, but the exceptional effects obtained with isoamyl alcohol may be due to its greater solubility in water and the consequently greater amount of this solute available for adsorption at the water-solid interface.

"Hysteresis" of Contact Angles.—The causes for the "hysteresis" of contact angles, that effect responsible for the existence of a definite advancing and a definite receding angle, have been obscure.³ A rational explanation of the "hysteresis" of contact angles can be made if it is assumed that formation of condensed layers does occur, and if, in addition, consideration is given to the fact that there is adsorption from the fluid phases in contact with the solid. The changes brought about at the various solid-liquid interfaces by adsorption and by the formation of condensed liquid layers would be sufficient to provide very different conditions at the line of contact of the phases when the water is caused to advance and when it is caused to recede. These different conditions account for the existence of stable advancing and stable receding angles. It is probable that both the advancing and the receding angles are equilibrium angles for the system as it exists at the moment of measurement, and that there is no single "equilibrium" angle for any system unless the system is so arranged that the

(3) Adam, "The Physics and Chemistry of Surfaces," Oxford Univ. Press, New York, N. Y., 1938, 2nd ed., p. 180.

same conditions prevail whether the water is advancing or receding.

During the course of this work it was demonstrated that for many systems one can obtain receding angles which have the same value as the advancing angles (including the stable advancing angles). This can be accomplished by permitting the solid to stand in contact with the organic liquid for a comparatively long period of time before forming the water drop, then by immediately receding the drop after its formation. It seems probable that the advancing angles (including the stable advancing angles) thus obtained are formed by water drops advancing over a condensed organic liquid layer, and that the receding angles are formed by water drops withdrawn before the water has an opportunity to remove the condensed organic liquid layer. If the water drop is allowed to stand it begins to remove the condensed layer and not only is the receding angle then obtained different from the advancing angle, but a new advancing angle, immediately reformed over the area that had been under the drop, is not the same as the advancing angle previously obtained.

With metal surfaces and other solid surfaces less inert chemically than gold and silver other complicating factors are introduced which affect the magnitude of contact angles and of interfacial contact angles. Studies carried out in this Laboratory on antimony, bismuth and cadmium have shown that for these more active substances still further factors must be considered in explaining differences between advancing and receding angles. The results of the work on antimony, bismuth and cadmium will be presented in a later paper.

Summary

1. With the sessile drop apparatus described in a previous paper interfacial contact angles were measured for water drops on silver and on gold immersed in organic liquids and for organic liquid drops on these solids immersed in water.

2. For each of the solid-organic liquid-water

systems it was possible to produce two stable and reproducible interfacial contact angles. These two angles have been designated as "stable advancing" and "stable receding" interfacial contact angles.

3. The stable advancing and stable receding interfacial contact angles given by water drops on silver and on gold immersed in organic liquids were the same (*i. e.*, within the limits of experimental error, 2° or less) as the corresponding angles obtained by using organic liquid drops on the solids in water.

4. The values of the stable advancing interfacial contact angles were found to be approximately the same for all the different organic liquids on a given metal, silver or gold. For silver this value was 128° and for gold 117° .

5. The stable receding interfacial contact angles were smaller than the stable advancing interfacial contact angles of the same system. For the non-polar organic liquids (benzene and heptane) the stable receding angles were practically of the same value against a given solid. For silver this value was 57.5° and for gold 45° . For the heteropolar organic liquids on silver and gold the stable receding contact angle values of the different liquids were not the same for a given solid but varied according to the solubility of the organic liquids in water. The greater the solubility of the organic liquids in water the larger were the stable receding angles.

6. The existence of two different stable interfacial contact angles for a given system has been explained by the theory that the solid surfaces, or interfaces, contiguous to the fluid phases become altered through adsorption from the fluids or by formation of condensed layers of fluid upon the surfaces. The experimental evidence obtained supports this view.

7. When a given system could be so acted upon by special manipulation that conditions at the interfaces were the same whether the water was advancing or receding, the water advancing angle was the same as the water receding angle.